REMOTE STORAGE

THE EFFECT OF THE AMOUNT AND NATURE OF EXCHANGEABLE CATIONS ON THE STRUCTURE OF A COLLOIDAL CLAY

by

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ABSTRACT

Electrodialyzed Putnam clay was saturated to different degrees with the basic cations, Li, Na, K, Mg, and Ca. Studies were made of the effects of these ions on the physico-chemical properties of this colloidal clay. The pH values of the clay were greatest according to the lyotropic series of cations: Li > Na > K > Mg > Ca > H. The monovalent cations increased the charge, dispersity, hydration and viscosity of the clay system. Maximum activity of these ions occurred at the point of saturation of the colloid. The divalent cations decreased these properties. Flocculation did not occur until the colloids were saturated with the divalent ions. The aggregates formed with Ca and Mg ions were large and weakly hydrated as compared with those formed with H ions. The size, stability and low hydration of the Ca- and Mg-aggregates are probably the important factors for producing and maintaining a good soil structure.

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The Effect of the Amount and Nature of Exchangeable Cations on the Structure of a Colloidal Clay

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Soil structure is referred to as the arrangement of the individual particles and aggregates of a soil. A soil is considered as having a good structure when its particles are aggregated into granules or crumbs which function more or less as a unit. Soils possessing such arrangements of the particles have a granular or crumb structure. They are rather porous and easily tilled. The maintenance of this type of structure is an important problem in soil management.

Zakharov[66]† introduces the term "structure capacity" of a soil, signifying the capacity of a soil to break up into aggregates. He emphasizes the degree of manifestation and stability (tenacity) of structure as being of prime importance in soil structure problems. This structure capacity of soils is dependent upon the relative amounts and the state of aggregation of the soil colloids.

Since the physical properties of soils are dependent to such a great extent upon the colloidal portion, the solution of the problem of providing and maintaining a good soil structure resolves itself into a more thorough understanding of the properties of the colloids. The fundamental observations made in a study of the structure and behavior of the colloids under different conditions may then be interpreted towards a better investigation of the soil complex as a whole.

The object of this investigation was to study the effect of exchangeable cations upon the properties of colloidal clay with the anticipation of finding out certain fundamental characteristics of the soil colloids that would lead to a better understanding of soil structure problems. It was hoped also that some of the observations made in a previous investigation of the relation of exchangeable cations to the physical properties of soils might be explained in light of these experiments[2]. This study includes: (1) the preparation of a series of clay sols containing various amounts of cations; (2) a study of the physico-chemical properties of these different sols in relation to the amount and nature of the exchangeable bases, involving the following measurements: (a) reaction and conductivity changes; (b) flocculation values; (c) migration velocities; (d) particle sizes; and (e) viscosity changes; and, (3) an interpretation of the relation of these results to the structure of soils.

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REVIEW OF LITERATURE

The effect of exchangeable cations on the structure of soils is distinctly evident from the wide differences in the properties of a soil saturated with Na and one saturated with Ca. Soils saturated with Na are sticky, viscous and highly dispersed when wet and hard when dry. Ca-saturated soils possess a more porous structure. Hissink[27], de Sigmond[15], Kelley and Brown[30], Gedroiz,[25] and others have shown that the colloidality of a soil, its physical properties and structure depend on the state of saturation of the soil and the nature of the exchangeable bases. Gedroiz[24] considers the soil exchange complex in a state of unsaturation with bases as representing gels of hydrophilic colloids. These colloidal substances, unsaturated or saturated with monovalent bases, are supposedly in a semi-reversible condition[23]. They pass into an irreversible state when saturated with the divalent ions. He observed that the dispersion of his soils followed the series:

$$Na > NH_4 > K > Mg > H > Ca > Ba$$

De Sigmond[16] found that soils saturated with Na were similar in their properties to Na-saturated, artificial zeolites. They possessed a puddled structure. A granular structure was produced by replacing Na with Ca. Best results were obtained when as many millimols of $CaSO_4$ were used as there were millimols of exchangeable Na_2O and K_2O in the zeolite. Gallay [22] states that for Ca to benefit the structure of a soil it must be added in excess of the total absorptive capacity. Hissink[27] reports that Ca produces flocculation when the soil is 95 per cent saturated with this cation. These differences are perhaps due to the method used for determining the absorptive capacity and to variations in the nature of the colloidal material.

Sokolovski and Lukaschewitsch[50] found that the resistance and plasticity of a soil were increased by replacing Ca with Na and NH_4. Ca- and Mg- saturated soils were loose, crumbling very easily. The resistance of soils, saturated with various cations, to pressure followed the series: $Na > NH_4 > Mg > Ca > H$. Mattson[40] observed that an electrodialyzed soil was more highly dispersed than the Ca-soil. Swelling of the colloidal material extracted from Sharkey clay was greatest according to the ionic order of $Na > Ca > H$. Charge followed the progression: $Na > H > Ca$. Anderson[1] reports that the heat of wetting and absorption of water by colloids saturated with various cations followed the order: $Ca > Mg > Na > H > K$. A different progression was observed for the effect of cations on swelling, moisture equivalent, migration velocity and pH, namely, $Na > K > Ca > Mg > H$. Anderson concludes that the influence of substituted cations on the properties of clay is usually directly proportional to the extent of their substitution. Mattson's results, however, do not support this conclusion.

Thomas[54] reports that soils saturated with various bases tend to be more highly, dispersed according to the ionic series: $Na > K > NH_4 > Ca > H$. He[55] also observed that the per cent of water in soils at low vapor pressures was higher according to the order: $Ca > H > Na > NH_4 > K$. Soil structure was influenced in a similar manner[53]. Parker and Pate[42] report that saturation of soils with monovalent bases causes a considerable reduction of the heat of wetting but that water absorption was practically unaffected.

Similar results were obtained by the author[2] in comparing the effect of different cations on the physical properties of soils. The Na- and K-saturated soils were found to have the lowest heat of wetting and moisture absorption, the K ion having the larger diminishing effect. These same soils were the most highly dispersed. The Na ion greatly increased the moisture equivalent values. The Na and K ions caused a lowering of the plasticity limits. The plasticity number of the Na-saturated soils increased; that of the K-soil decreased. Ca-saturated soils, containing a large percentage of clay, were distinctly flocculated. These observed effects of the various cations were not explained because of the lack of a sufficient understanding of the effect of these ions on the colloidal portion of the soil. These data, in addition to that of other workers, show the need of more investigations concerning the nature of these phenomena.

PREPARATION OF MATERIALS

Soil from the heavy layer of the Putnam silt loam was used throughout this investigation. The colloidal fraction was isolated according to the method of Bradfield[5], with the exception that the soil was originally saturated with Na in order to promote a higher degree of dispersion. The extracted colloid was electrodialyzed in a three-compartment cell until free from exchangeable cations and anions[8]. The purpose of this electrodialysis was to prepare a clay system that would be as pure as possible so that the ion on the absorbing complex could be rather accurately determined and controlled.

The electrodialyzed clay was thoroughly dispersed in distilled water by means of prolonged stirring and shaking. The concentration was determined with a pyknometer and the stock solution diluted to contain 3.4 per cent by weight of colloid. The specific gravity of the clay was found to be 2.78. The saturation capacity of the clay for bases was determined according to the conductometric and potentiometric methods suggested by Bradfield[7]. This value was 57 milliequivalents per 100 grams of clay, confirming all previous results obtained with this particular clay.

The H-clay was then saturated with different amounts of the various cations by adding the ion in the form of the hydroxide. This reaction produces a clay containing the cation of the base on the exchange complex without the introduction of an anion except the OH ion which forms water with the H ions replaced from the clay. The reaction involved in this procedure is expressed by the equation:

$$\text{H-clay} + \text{NaOH} \rightleftharpoons \text{Na-clay} + \text{HOH} \quad (1)$$

This method provides a means of preparing different clay systems with a high degree of purity with respect to the added cations. Leaching with neutral salts has been the most widely used method for saturating clays with various cations. However, this method has two major disadvantages: (1) the addition of an anion which cannot be removed from the system, and (2) the inability to rather definitely control the quantity of cations on the colloid. The anion effect in the behavior of colloidal systems has often been overlooked in the interpretation of results.

Different amounts of the hydroxides of Li, Na, K, Ca and Mg were added to this 3.4 per cent H-clay suspension in order to obtain a series of clay sols that were 25, 50, 75 and 100 per cent saturated with the various bases. These respective degrees of saturation correspond to 14.25, 28.50, 42.75 and 57 milliequivalents of base per 100 grams of clay. Several additional suspensions were prepared, representing the quantity of cations necessary to produce flocculation. In the case of the monovalent cations a series of sols was prepared to contain one-half of this minimum electrolyte requirement. These data provided for a number of suspensions containing: 67 milliequivalents of each of the cations, 108 and 217 milliequivalents of K, and 218 and 536 milliequivalents of Li and Na per 100 grams of colloid.

The bases were added slowly with constant stirring of the suspension in order to insure a uniform distribution of the cations throughout the colloidal clay. Rapid addition of the bases, especially $Ca(OH)_2$ and $Mg(OH)_2$, results in local areas having a higher concentration of ions than the remaining sol. This tends towards localized flocculation of the clay. The final concentration of these prepared sols was 2.3534 per cent by weight of clay. They were kept in Pyrex flasks, tightly stoppered with paraffined corks.

REACTION AND SPECIFIC CONDUCTIVITY STUDIES

The Effect of Various Bases on the Reaction of Colloidal Clay.—The change in reaction of these clays as a function of the amount and nature of the exchangeable bases on the absorbing complex was measured by

TABLE 1.—SPECIFIC CONDUCTIVITY AND pH VALUES OF COLLOIDAL CLAY CONTAINING DIFFERENT AMOUNTS OF EXCHANGEABLE CATIONS

Ion	Milliequivalents per 100 grs. clay	pH		Specific conductivity mhos x 10^5	
		sol	ultra-filtrate	sol	ultra-filtrate
H	57.00	3.61	----	5.00	4.00
Li	14.25	5.52	----	4.70	----
	28.50	6.10	----	6.96	----
	42.75	6.45	----	9.12	----
	57.00	6.95	----	14.66	----
	67.00	8.12	----	21.90	----
	218.00	>10.00	----	477.00	----
	536.00	>10.00	----	1,342.00	----
Na	14.25	5.26	6.75	5.58	4.7
	28.50	5.71	6.80	8.26	6.4
	42.75	6.07	6.90	10.71	7.2
	57.00	6.75	7.00	18.23	12.9
	67.00	7.99	7.40	25.51	17.0
	80.00	8.80	----	45.58	----
	218.00	>10.00	----	563.60	----
	536.00	>10.00	----	1,581.00	----
K	14.25	5.03	----	4.54	----
	28.50	5.52	----	6.32	----
	42.75	5.96	----	7.60	----
	57.00	6.50	----	15.34	----
	67.00	7.34	----	20.40	----
	80.00	7.90	----	39.50	----
	108.87	>10.00	----	100.02	----
	217.75	>10.00	----	469.30	----
Ca	14.25	4.36	5.60	4.40	3.90
	28.50	4.79	6.20	3.70	3.78
	42.75	5.28	6.50	3.80	4.00
	57.00	5.95	7.10	6.90	6.00
	67.00	6.95	7.30	13.90	13.00
Mg	14.25	4.50	----	3.71	----
	28.50	4.97	----	3.58	----
	42.75	5.31	----	3.87	----
	57.00	6.19	----	8.37	----
	67.00	6.98	----	16.53	----

means of the quinhydrone and hydrogen electrodes. The clay sols containing the monovalent ions had a poisoning effect on the hydrogen

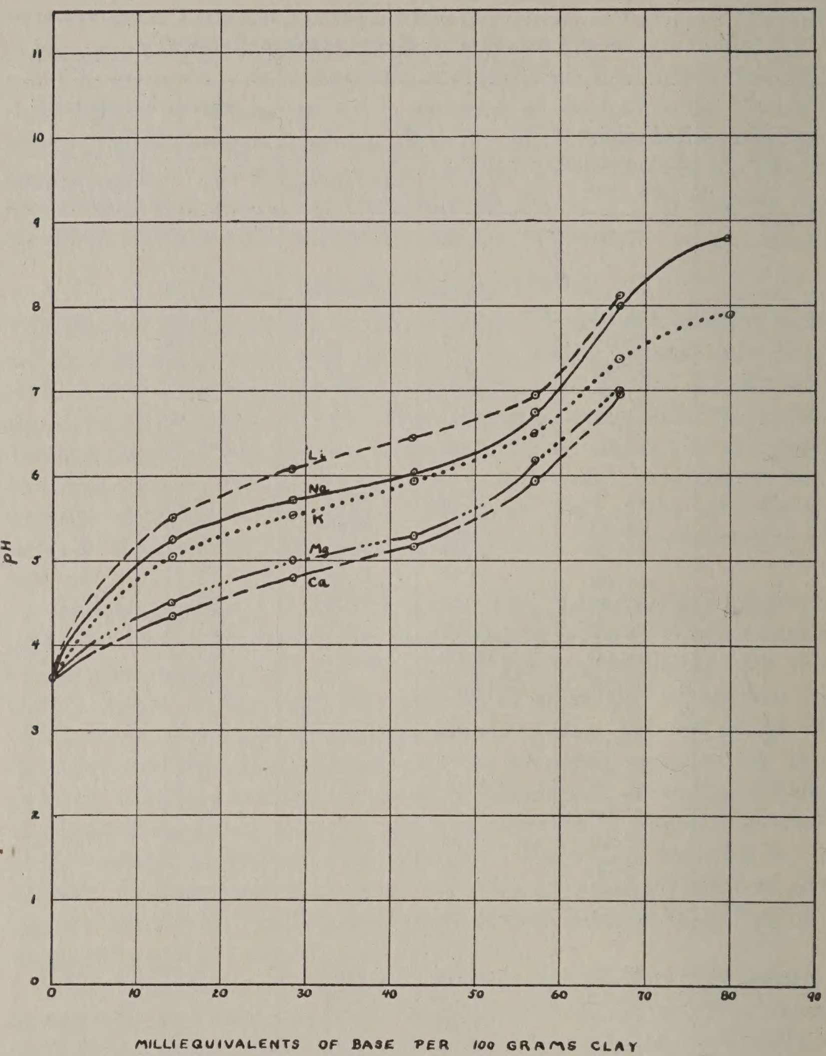

Fig. 1.—The change in reaction of clays containing various amounts of different cations.

electrode above pH 7.0. The quinhydrone electrode exhibited large deviations above pH 9.0. Therefore, the pH values of the highly alkaline clays could not be satisfactorily measured. In this case the results were recorded as > pH 10.0. The recorded observations represent quinhydrone electrode readings.

The pH values of these sols and of the ultrafiltrates from the Ca- and Na-clays, are given in Table 1. Titration curves are shown in Fig. 1.

The results confirm the acid nature of this clay as reported by Bradfield[4]. The clay is strongly buffered throughout most of the pH range. The lyotropic effect of the added cations is very evident from these curves. The Li ion, with its high hydration, is loosely bound to the particle thereby undergoing a surface dissociation, greater than any of the other less hydrated ions, causing a larger increase in the pH values. The dissociation tendency increases with hydration according to the series: Li>Na>K for the monovalent cations and Mg>Ca for the divalent. Anderson[1] reports a similar series for the pH values of clay saturated with different ions, except that the Ca-clay had a slightly higher pH than that of the Mg-clay. His clays, however, were saturated by leaching the soils with the chlorides of neutral salts and the inability of removing all of the chlorides may account for this difference.

These curves exhibit a distinct inflection point at about 62 milliequivalents of base per 100 grams of clay indicating the point of neutralization of the exchangeable H ions. This value is about 9 per cent higher than the original saturation point determined by immediate titration of the clay sol. However, these values were obtained after the base had been added to the clay and the suspension allowed to stand for about three months. This change suggests that a diffusion of the cation into the particle probably takes place, neutralizing H ions that are not upon the immediate surface of the colloid. The pH values resulting from the saturation of any particular colloidal clay is undoubtedly dependent upon the nature of that clay. Anderson[1] has shown that this relationship appears to be a function of the SiO_2-sesquioxide ratio.

Specific Conductivity of Clay Sols Containing Different Amounts of Bases.—The conductivity measurements were made in a conductivity cell having a constant of 0.062. All determinations were carried out in a thermostat at 25° C. The conductivity data are shown in Table 1 and Fig. 2. These curves are characterized by a break at about 59 milliequivalents, indicating the point at which all the exchangeable H ions have been replaced from the particles.

The points above the Li-, and Na-, and K-clay curves represent an hydrolysis effect, signifying that there has been an increase in the number of ions in solution. This increase is only apparent with the monovalent cations. The insolubility of the clay salts saturated with the divalent ions causes a different type of curve. Bradfield[7] has suggested that bases with divalent cations are not suitable for the conductometric determination of the saturation capacity because of these effects.

Conductivity measurements are being used by Pauli and his students to characterize the nature of various colloidal systems. Pauli and Schmidt[44] have found that the conductivity of an $Al(OH)_3$ sol, stabilized with the chloride ion, when titrated with $AgNO_3$, increases sharply

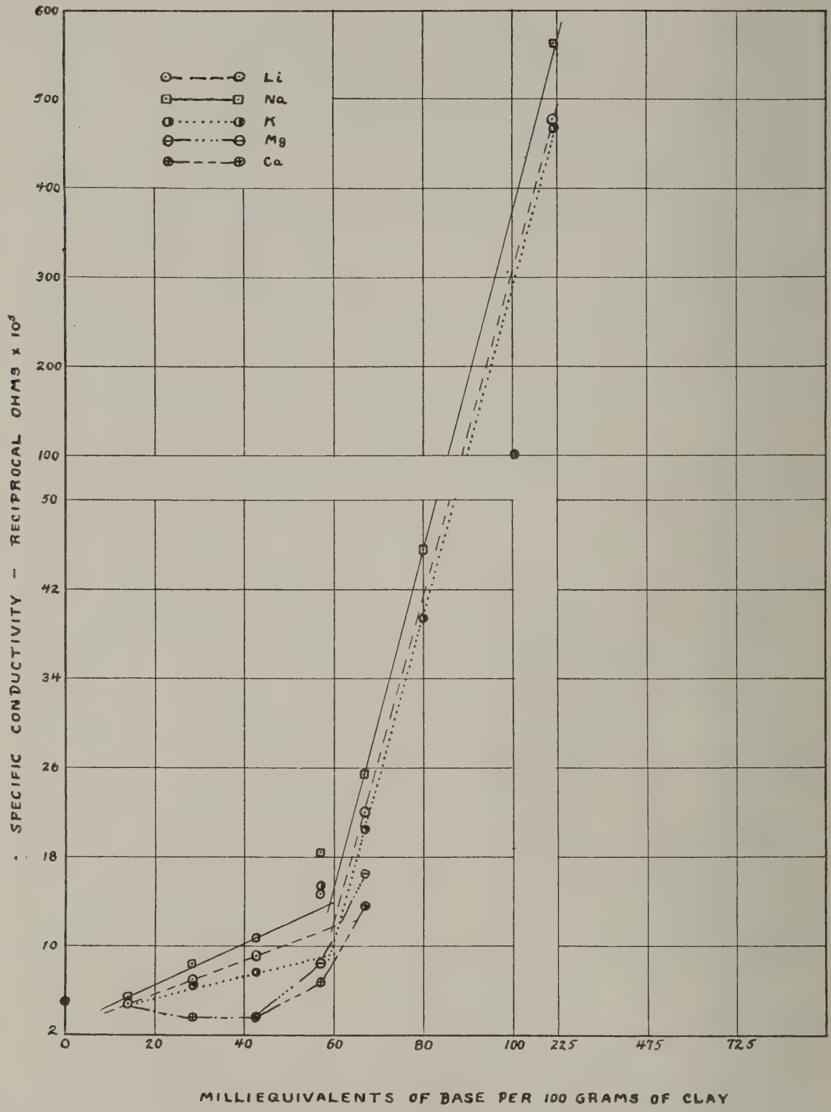

Fig. 2.—Specific conductivity of clays containing different amounts of bases.

at a point corresponding to the analytically determined Cl content of the sol. All of the stabilizing electrolyte was exchangeable. Rabinowitsch and Dorfmann[46] observed a similar effect with the As_2S_3 sol when titrated with $BaCl_2$. The point at which all of the H ions had been replaced from the colloid by the cation of the neutral salt was found to be independent not only of the concentration of the salt but also of the valency of the replacing ion, except in the case of hydrolyzable salts.

The conductivity curves of Li-, Na-, and K-clays exhibit an apparent discrepancy with regards to hydration, since the conductivity is greater according to the series: Na>Li>K. However, two different factors must be considered in these effects, the degree of dissociation of the different clays and the mobility of the ions resulting from this dissociation. The dissociation of these clays follows the order: Li>Na>K. There will be more Li ions in solution than Na and K ions. The Li ion, with its high hydration, has the lowest mobility. The K cation has the greatest. Therefore, the nature of the conductivity curves will be dependent not only upon the amount of a particular ion but also upon its mobility. In this way, the Li-clay possesses a conductivity that lies between that of the Na- and K-clays.

The conductivity of the ultrafiltrate of the Ca-clays is not appreciably different from that of the sol. However, as the concentration of Na ions in the Na-clay system increases, the conductivity of the intermicellar liquid becomes greater, denoting an hydrolysis of the Na-clay. Similar results have been reported by other investigators. Kruyt and van der Willigen[33] found that the conductivity of the ultrafiltrate as compared with that of the sol varied considerably from one colloid to another. The ultrafiltrate of the HgS and Au sols was not materially different from that of the sol itself. The conductivity of the As_2S_3 ultrafiltrate varied from 10 to 40 per cent lower than that of the sol, depending upon the concentration. Wintgen and Weisbecker[64] observed that the conductivity of the ultrafiltrate of the $Cr(OH)_3$ sol varied from about 5 to 10 per cent from that of the sol itself.

These conductivity and reaction data clearly show that there is an increase in the concentration of ions in solution at the point of saturation of the colloidal clay. This point of saturation represents complete neutralization of the H ion on the exchange complex.

FLOCCULATION

The flocculation values were determined by adding successive amounts of bases to the H-clay, keeping the final concentration equal to 2.3534 per cent. Small test tubes were used in these experiments. The suspensions, containing the added bases, were vigorously shaken, allowed to stand over night, shaken again the next morning and then centrifuged for 15 minutes. The flocculation values represent an error from the minimum electrolyte requirement of about 5 per cent. These values are given in Table 2 and are expressed as milliequivalents of base per 100 grams of clay on the basis of a 2.3534 per cent by weight suspension.

These results distinctly show the effects of the valency and hydration of ions on the flocculation of colloidal clay. The flocculation value for the K ion is approximately one-half that for the highly hydrated Li and Na ions. Tuorila,[58] observed that the minimum electrolyte require-

TABLE 2.—FLOCCULATION VALUES OF COLLOIDAL CLAY SATURATED WITH VARIOUS CATIONS. FINAL CONCENTRATION OF SOL = 2.3534 PER CENT BY WEIGHT OF COLLOID

Flocculating cation	Li	Na	K	Ca	Mg
Minimum electrolyte requirement in milliequivalents of base per 100 grs. of clay	536	536	217.75	67	67

ment for a clay sol was about the same for LiCl and NaCl but that the amount of KCl necessary for flocculation was about two-thirds less. The divalent ions flocculate at a much lower concentration. The sols flocculated with the monovalent ions were highly viscous, gelation taking place as the suspensions aged. This effect was undoubtedly due to the high concentration of ions that was required to produce flocculation and to the particular concentration of clay. Flocculation in these alkaline mediums magnified the hydration changes brought about by coagulation.

Bradfield[6] has definitely shown that there must be an excess of cations in the intermicellar liquid above the saturation capacity of the colloid in order to decrease the charge on the particle and produce flocculation. Rabinowitsch and Dorfmann[46] have shown that equivalent quantities of different cations are required to replace the H ions from the As_2S_3 sol but that the excess of cations in the intermicellar liquid, necessary to produce flocculation, depends upon the valency and hydration of these ions. This point is confirmed by the results with this colloidal clay. The divalent cations flocculated the clay when the excess of these ions was about 17.5 per cent above the saturation point. This amount was 282 and 840 per cent above saturation with the K and the Li and Na ions, respectively. Hissink[27] reports that clay is in a flocculated condition when the absorbing complex is 95 per cent saturated with Ca. Gallay's[22] and de Sigmond's[16] results indicate that flocculation takes place either at the saturation point or slightly above it. The data discussed above confirm these observations, showing that there must be an excess of ions in the intermicellar liquid before flocculation ensues.

CATAPHORESIS

Historical

The stability of a colloidal system is dependent upon the charge and hydration of the particles, depending upon the nature of the colloid. The charge on the particle is the sole factor determining the stability of hydrophobic colloids. Both charge and hydration are responsible for the stability of lyophilic sols. Removal of the charge from the colloidal particles results in coagulation. Powis[45] has shown, however, that the charge does not have to be entirely removed in order to produce flocculation. A lowering of the electrokinetic potential to a certain value, which he calls the "critical potential", is sufficient to bring about flocculation.

The ion of opposite charge to that of the particle is responsible for this lowering of the potential. This indicates that the electrokinetic potential is due to the ions held on the surface of the particles. These ions may be absorbed by the particle or they may arise from the particle by surface dissociation. Wiegner[62] considers the charge of the clay particles as arising from the dissociation of ions from the clay colloids. The highly complex anions of silicic acid or of various silicates are retained by the unsaturated valences of the surface Al- atoms of the clay. These ions form the inner layer, producing the negative charge of the clay. Bradfield[4] considers the charge as arising from a dissociation of ions directly from the surface of the clay particle.

The exchangeable cations form the outer layer of the particle. The charge on the particle will be greater as the hydration of these cations is larger. Irrespective of the nature of the inner layer, the charge will increase with increasing hydration of the ions of the outer layer according to the ionic series:

$$\mathrm{Li} > \mathrm{Na} > \mathrm{K} > \mathrm{Rb} > \mathrm{Cs}$$

$$\mathrm{Mg} > \mathrm{Ca} > \mathrm{Sr} > \mathrm{Ba}$$

Briggs[10] holds a similar view in regards to the origin of the potential in cellulose membranes. He states that the potential existing across the interface may be due to ions set free at the surface of the solid phase but that this potential will be governed by all of the ions present in the system. Mattson[38] has shown that the charge on soil colloids varies markedly according to the nature of the exchangeable base present. The amount of the exchangeable bases should have an effect on the charge of the particle as well as the nature of these bases.

Experimental

Method Used.—Measurements of the charge of colloidal particles fall into three different groups: (1) the rate of movement of a boundary between the colloidal suspension and the clear dispersion medium, (2) the rate of change in concentration of the dispersed phase in a certain volume near the boundary measured, and (3) the velocity of the individual particles measured in an ultramicroscope. The first method, represented by the Burton U-tube, has been used more extensively because of its simplicity. However, this method is not entirely satisfactory. A distinct boundary between the sol and ultra-filtrate is often very difficult to obtain. The difference in the conductivity of the suspension and the dispersion medium; the effects of electrolysis and polarization; and the changes in the concentration of the different ions in the system introduce sources of error in the determinations.

Direct ultramicroscopic measurements overcome most of these difficulties. However, these determinations, depending upon the technique used, may be subject to large errors due to the disturbing action of the products of electrolysis and the warming of the liquid by the electric current. Tuorila,[59] has devised a simple cell for use with the ultramicroscope that reduces these errors to a minimum. The cell employed in this investigation was built according to his original suggestions with the exception that a soft grade of DeKhotinsky cement was used instead of "picein", thereby making a cell of higher rigidity. The open type of cell was selected in preference to the closed. The final dimensions of the cell were 40 x 26 x 1.812 mm. A detailed, illustrated description of the method for building this cell is given in Tuorila's original paper.

This cell has several advantages for ultramicroscopic work. The optical properties are excellent since the walls are parallel producing no reflection of the beam of light. Measurements can be made in the middle of the cell. The disturbing action of the products of electrolysis can be eliminated by frequent changing of the solutions. The solutions can be drawn from the cell through the open side by means of a filter paper. It has two disadvantages that must be guarded against in its use. The cell cannot be cleaned easily. If a chromic acid mixture is allowed to stand in the chamber too long it attacks the cement perhaps producing a leak. However, it can be thoroughly cleaned by washing it out with a soap solution. This can be accomplished by placing a thin cloth over a spatula that has been ground square on one end and rubbing the inside of the cell as gently as possible with the cloth saturated with the soap. After this treatment, a fine jet of water is sprayed into the cell for about 5 minutes. This rinsing removes all of the soap solution and leaves the glass perfectly clean. This process need not be repeated more than twice daily depending upon the number of determinations that have been made. A cell with clean walls is very important in ultramicroscopic cataphoresis measurements. Any material adsorbed on the wall will affect the potential. The other difficulty is the disturbing currents that may be produced by evaporation of water from the open side of the cell. These currents cause the particles to move diagonally across the field when observations are being made. This is easily overcome, however, by applying a thin coat of paraffine on the bottom of the cell at this open side. The paraffine keeps the layer of water within the cell and thereby reduces evaporation to a minimum. The introduction of any light that may contain heat waves will also produce convection currents. These disturbing influences were found to be more numerous in cells having a depth greater than 2 mm.

The optical arrangement used in this investigation was that of the slit ultramicroscope of Siedentopf and Zsigmondy. A saturated solution of alum was placed in the path of the beam of light to absorb the heat. The microscope used for making the observations had a 16 mm objective and a 17.5 eyepiece giving a magnification of 175 diameters.

The potential difference at the electrodes was 20 volts. This corresponded to a potential fall of 5 volts/cm.

The cataphoretic velocity of the particles was measured in both directions with a stop watch. The current was reversed by means of a commutator on the average of about 5 to 10 seconds. The solution was changed after making 5 observations. The movement of the particles in both directions was not always the same, the velocity in any one direction being constant. Tuorila,[59] has shown that the mean of the rapidities in both directions gives correct results. The experimental error in making these observations was about 5 per cent.

Velocity of Particles at Different Depths in the Cell Used.—Observed movement of the particles at different depths in the cell is different. They move in opposite directions in the middle and near the walls. These effects are due to the electroendosmotic flow of the water, brought about by the negative charge of the glass walls. Water moves along the walls towards the cathode. Since the cell is closed between the electrodes as much water as flows along the walls in one direction must flow back through the center of the cell in the opposite direction. Therefore, the observed velocity of the particles is equal to the true velocity of the particle plus the velocity of the liquid.

$$z=u+v \tag{2}$$

where

z = observed apparent velocity of the particles.
u = true cataphoretic velocity of the particles.
v = electroendosmotic velocity of the water.

Smoluchowski[48] has developed a formula for the electroendosmotic velocity of water in a thin cell. This formula is

$$v=v_o\left(1-6\left(\frac{s}{L}-\frac{s^2}{L^2}\right)\right) \tag{3}$$

The velocity of the particles would then be

$$z=u+v_o\left(1-6\left(\frac{s}{L}-\frac{s^2}{L^2}\right)\right) \tag{4}$$

where

v_o = electroendosmotic velocity of the water at the wall of the cell.

L = thickness of the cell.

s = distance from the wall where the true velocity of the particle takes place.

The expression in brackets will equal zero when

$$\frac{s}{L}=\frac{1}{2}-\frac{1}{\sqrt{12}} \qquad (5)$$

Therefore, the true velocity, u, is found at a depth equal to 0.2113L. Also according to Smoluchowski,

$$u=\tfrac{3}{4}z_{1/6}+\tfrac{1}{4}z_{1/2} \qquad (6)$$

where

$z_{1/6}$ and $z_{1/2}$ refer to the observed velocities at a distance $1/6$ and $1/2$ of the depth of the cell away from the wall.

With these considerations in mind, the apparent velocity of the particles in a suspension of clay was measured at different depths of the cell. These values are given in Table 3. The curve showing the cataphoretic velocity of the particles with respect to depth in this particular cell is shown in Fig. 3. The true velocity of the particles calculated at a depth of 0.2113 L is equal to 3.4 microns/sec. That calculated from equation 6 is equal to 3.41 microns/sec. The observed velocity of the particles next to the wall was found to be too large to fall on the theoretical curve. This effect was also observed by Tuorila. It is probably due to an unevenness of the wall or to adsorption effects on the wall. However, the velocities a short distance from the wall are not subject to these errors and therefore fall on the curve as calculated by Smoluchowski's formula.

TABLE 3.—CATAPHORETIC VELOCITY OF CLAY PARTICLES AT DIFFERENT DEPTHS IN THE CELL. POTENTIAL GRADIENT, 5 VOLTS/CM.

Distance from top of cell microns	35	50	225	325	386	725	875	1100
Velocity of particles microns per sec. per volt per cm.	−2.63	−2.02	+2.50	+3.10	+3.27	+5.20	+5.25	+5.00

The cataphoretic velocities of the particles are usually expressed in microns/second at a potential fall of one volt/cm. The electrokinetic potential, zeta, can be calculated from these velocities with the Helmholtz-Perrin equation:

$$\text{zeta} = \frac{4\pi\ \eta v(300)\ (300)}{HD} \tag{7}$$

where

v = velocity of the particles.
H = fall in potential in volts/cm.
D = dielectric constant of water.
η = viscosity of water.
300 x 300 = factors for converting H and zeta from electrostatic to absolute units.

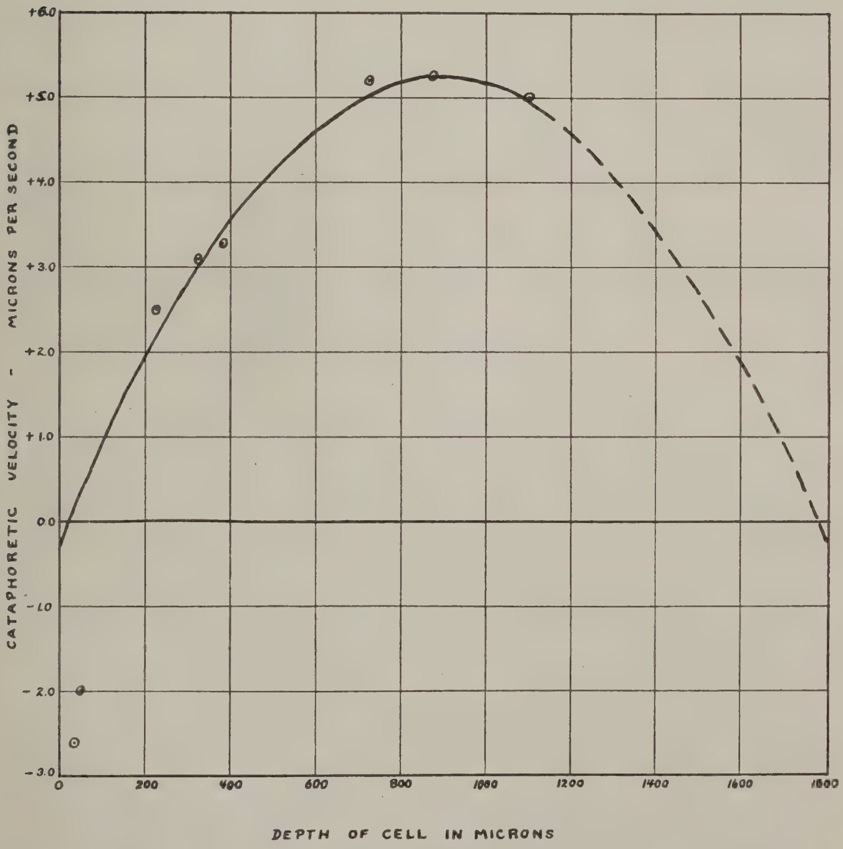

Fig. 3.—Migration velocity of clay particles at different depths of the cell.

The Effect of the Fall in Potential Upon the Migration Velocity.—The fall in potential used in cataphoresis experiments has varied from one investigator to another. Tuorila recommends a potential gradient of 3 volts/cm for this type of cell. Freundlich and Abramson[21] report that the cataphoretic velocity of red blood corpuscles in serum was directly proportional to the fall in potential. A similar effect was observed with zinc dust particles in gelatin. In order to determine if their results were applicable to the velocity of clay particles, the migration velocity of this colloidal clay was studied at different potential gradients. Two different cells were used having a distance of 3.5 and 4 cm between the electrodes. These observations are shown in Table 4 and Fig. 4.

Table 4.—The Effect of the Fall in Potential Upon the Cataphoretic Velocity of Clay Particles

	Volts applied	Fall in potential volts per cm.	Velocity of particle microns per second
Cell No. 1	10	2.5	12.32
electrodes 4 cm. apart	20	5.0	22.35
	30	7.5	30.50
	40	10.0	40.50
	50	12.5	55.50*
Cell No. 2	10	2.66	7.40
electrodes 3.5 cm. apart	20	5.32	21.00
	30	7.98	29.50
	40	10.64	43.50
	50	13.30	74.00*

*electrolysis effects

The data confirm the work of Freundlich and Abramson up to a fall in potential of 10 volts/cm. Above this point, electrolysis effects in this small cell become a limiting factor and the velocity of the particles increased more rapidly than the potential gradient. However, a fall in potential of 10 volts/cm is considerably higher than that generally used in making cataphoresis measurements.

Migration Velocity as Affected by Dilution.—Since the charge on the colloidal particle is associated with the ions in the outer layer of the particle , the migration velocity should become greater as surface dissociation of these ions on the particle increases. Valko and Weingarten[60] observed that the Cl activity and the migration velocity of the Al $(OH)_3$ sol increased with dilution. Bradfield[4] has shown that the ionization of this acid colloidal clay increases with increased dilution.

The migration velocity of this clay, saturated with H ions, was determined at different concentrations of the sol. The concentrations

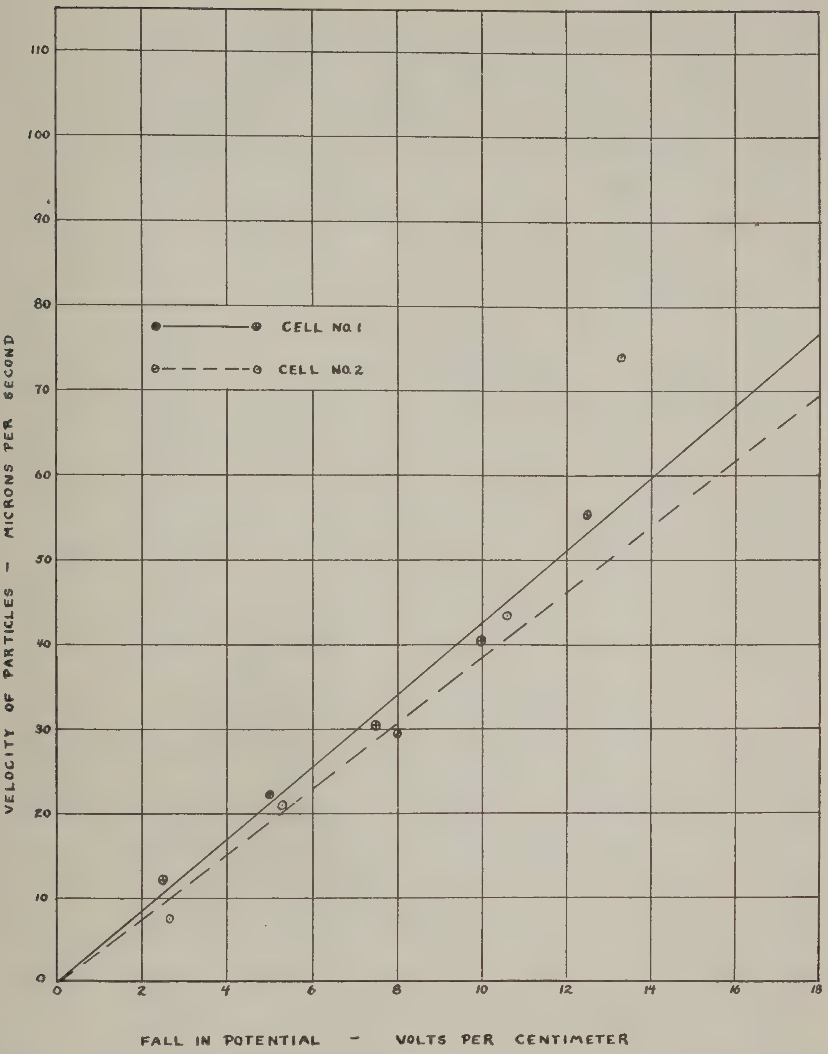

Fig. 4.—The effect of the fall in potential upon the migration velocity of clay particles.

were chosen to cover the range that could be used in the ultramicroscope. These results are given in Table 5, along with the pH values of the solutions. There is an increase in the velocity of the particles with dilution up to a certain concentration. The pH values follow a similar course. These values are of the same order of magnitude as those observed by Valko and Weingarten and indicate that the migration velocity of the colloid is a function of the dissociated ions on the particle.

TABLE 5.—THE EFFECT OF DILUTION ON THE CATAPHORETIC VELOCITY OF H-CLAY. POTENTIAL GRADIENT, 5 VOLTS/CM.

Concentration of clay grams per liter	Cataphoretic velocity microns per sec. per volt per cm.	pH
0.11775	2.30	5.52
0.05887	2.48	5.77
0.02826	2.62	6.08
0.01884	2.60	6.05
0.00942	2.67	6.05

The Relation of Exchangeable Cations to Migration Velocity.—The electrokinetic potential of colloidal particles is greatly influenced by electrolytes. The curves giving the relation between charge and electrolyte concentration generally exhibit a maximum with the mono- and divalent ions at low concentrations, then decreasing as the concentration of these ions increases. These relationships are fully discussed by Svedberg,[51] and Kruyt[31]. Tuorila[58] studied the effect of different electrolytes on the migration velocity of clay sols and found that the cataphoretic velocity was lowered according to the following electrolyte and cation series:

$$LiCl < NaCl < KCl = AgNO_3 < CsCl < HCl$$
$$MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$$

There was a slight increase in these velocities with small additions of the monovalent chlorides, LiCl, NaCl and KCl. The divalent chlorides and HCl caused an immediate decrease in the velocity of the particles. The clay suspensions, however, were not freed from exchangeable bases before treating with the various electrolytes. Mattson[40] reports that the migration velocity of electrodialyzed clay and bentonite increases by saturating these colloids with Na and decreases when Ca is the saturating ion. He finds that the electrokinetic potential reaches a maximum before 100 per cent saturation with Na. Anderson[1] observed that the colloids saturated with H ions have a lower potential than those saturated with Ca. However, he extracted the soil with HCl to bring about saturation and the presence of the Cl ions probably accounts for this difference.

The migration velocity of the clay sols used in this investigation was determined by the method described above with a potential gradient of 5 volts/cm. The solutions were changed after having made 5 observations. The relation of the amount and nature of the exchangeable bases to the velocity of the clay particles is shown in Table 6 and Fig. 5. The cataphoresis curves show very markedly the effect of the valency of the cation on the charge of the clay particle. The effect of hydration

TABLE 6.—THE RELATION OF THE AMOUNT AND NATURE OF EXCHANGEABLE BASES TO THE VISCOSITY AND CHARGE OF COLLOIDAL CLAY

Ion	Milli-equivalents per 100 grs. clay	Viscosity		Migration velocity microns per sec. 1 volt per cm.	Zeta-potential milli-volts
		time in seconds	relative viscosity		
H	57	64.7	1.4232	2.70	34.3
Li	14.25	62.2	1.3683	2.86	36.4
	28.50	67.2	1.4787	3.04	38.7
	42.75	68.4	1.5048	3.25	41.3
	57.00	63.5	1.3969	3.53	44.9
	67.00	61.0	1.3420	2.96	37.6
	218.00	81.4	1.7906	3.00	38.2
	536.00	280.0	6.1600	----	----
Na	14.25	61.4	1.3506	2.73	34.7
	28.50	65.0	1.4298	2.97	37.8
	42.75	67.2	1.4787	3.19	40.6
	57.00	63.2	1.3903	3.57	45.4
	67.00	60.6	1.3330	2.86	36.4
	80.00	58.0	1.2759	2.80	35.6
	218.00	58.2	1.2809	2.88	36.6
	536.00	230.0	5.0600	----	----
K	14.25	57.8	1.2715	2.68	34.0
	28.50	60.2	1.3243	2.88	36.6
	42.75	64.2	1.4123	3.21	40.8
	57.00	64.2	1.4123	3.47	44.1
	67.00	62.2	1.3683	2.70	34.3
	80.00	59.0	1.2980	2.67	34.0
	108.87	57.9	1.2737	----	----
	217.65	190.0	4.1800	----	----
Ca	14.25	61.0	1.3420	2.39	30.4
	28.50	57.4	1.2627	2.32	29.5
	42.75	56.4	1.2407	2.19	27.9
	57.00	56.6	1.2450	2.11	26.8
	67.00	61.0	1.3420	2.08	26.5
Mg	14.25	57.1	1.2560	2.50	31.8
	28.50	56.4	1.2407	2.45	31.1
	42.75	56.4	1.2407	----	----
	57.00	56.4	1.2407	2.32	29.5
	67.00	60.0	1.3200	2.31	29.4

of the ions is not very strongly expressed. However, the lyotropic effect of the ions is present. The curves for the monovalent cations are charac-

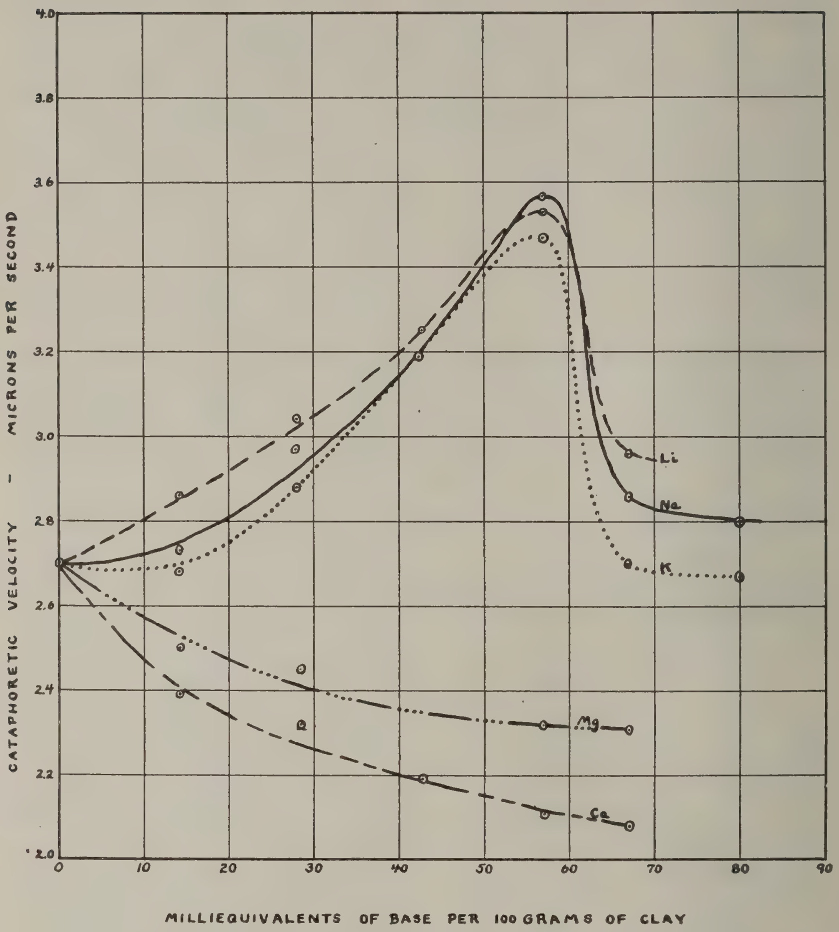

Fig. 5.—The migration velocities of clay sols as affected by the amount and nature of exchangeable cations.

terized by an initial increase in the migration velocity up to a maximum where they fall off sharply to a more or less constant value as the concentration of the ions in the system increases. This maximum point is reached at the saturation capacity of the colloid for bases, indicating that the maximum activity of the ions on the particle, exerting their effect on the migration velocity is reached at this value. Mattson[40], however, reaches this maximum point before complete saturation of the colloid. The sharp decrease in the velocities can be explained by considering the higher concentration of ions in solution as suppressing the effect of the ions on the particle. In other words, there is a repression of the ionization of the particular clay salts. As the concentration of ions in the solution increases this repression of ionization becomes greater, reducing the number of "active ions" on the surface of the particle. This causes a sharp decrease in the charge on the particle.

The slight differences between the velocities affected by the different monovalent cations has also been observed by Tuorila. Buzagh[11] reports a similarly shaped curve for electrodialyzed bentonite when treated with increasing quantities of NaOH.

The divalent cations cause a gradual decrease in the charge on the particles as the concentration of these ions increases. This effect appears to be more or less universal in cataphoretic phenomena. It is probably due to the low dissociation of the Ca- and Mg-clays. A smaller number of ions on the particle as well as a lower activity of these ions should be expected to cause a decrease in the charge on the particle.

The critical potential for the Li-, Na- and K-clays is 38.2, 36.6 and 34.0 millivolts, respectively. This value for the Ca- and Mg-clays is 26.5 and 29.4. The H-clay with a potential of 34.3 millivolts is very close to the critical value since the H-saturated sol is nearly flocculated. Tuorila found the critical potential for his particular clay suspension to be 48 millivolts for the monovalent cations and 45-46 millivolts for the divalent. The critical potential undoubtedly varies with the chemical composition of the colloidal clay. For any particular clay, the critical value will depend upon the nature of the flocculating agent.

SIZE OF PARTICLES

Ultramicroscopic Method

In order to study the change in dispersion of the H-clay sol when treated with monovalent and divalent cations, the size of the particles of the Na- and Ca- series of clays were determined in the ultramicroscope. Any change in the size of the particles, which undoubtedly included small aggregates in many instances, would signify a change in the degree of dispersion. Ultramicroscopic counts were made with these clay sols, diluted with their ultrafiltrates. In this way the concentration of electrolytes in the system could be maintained as constant as possible.

The ultrafiltrates were obtained with the use of a pressure ultrafilter under a pressure of 100 pounds per square inch. Collodion membranes were used to hold back the colloidal particles. The membranes were made by allowing layer a of collodion to harden in a petri dish. This technique produced a membrane that proved to be very efficient for ultrafiltering these clay sols. 100 cc of the sol were filtered, furnishing a sufficient quantity of ultrafiltrate for making these counts. 500 counts were made with each sol, using the same Siedentopf and Zsigmondy

TABLE 7.—THE EFFECT OF EXCHANGEABLE CA AND NA UPON THE SIZE OF PARTICLES IN COLLOIDAL CLAY

Milliequivalents of base per 100 grams of clay	Size of particles radius in millimicrons	
	Ca	Na
0	136	136
14.25	126	113
28.50	122	96
42.75	121	98*
57.00	130	96*
67.00	148	---
536.00	---	110

*All particles not visible in ultramicroscope.

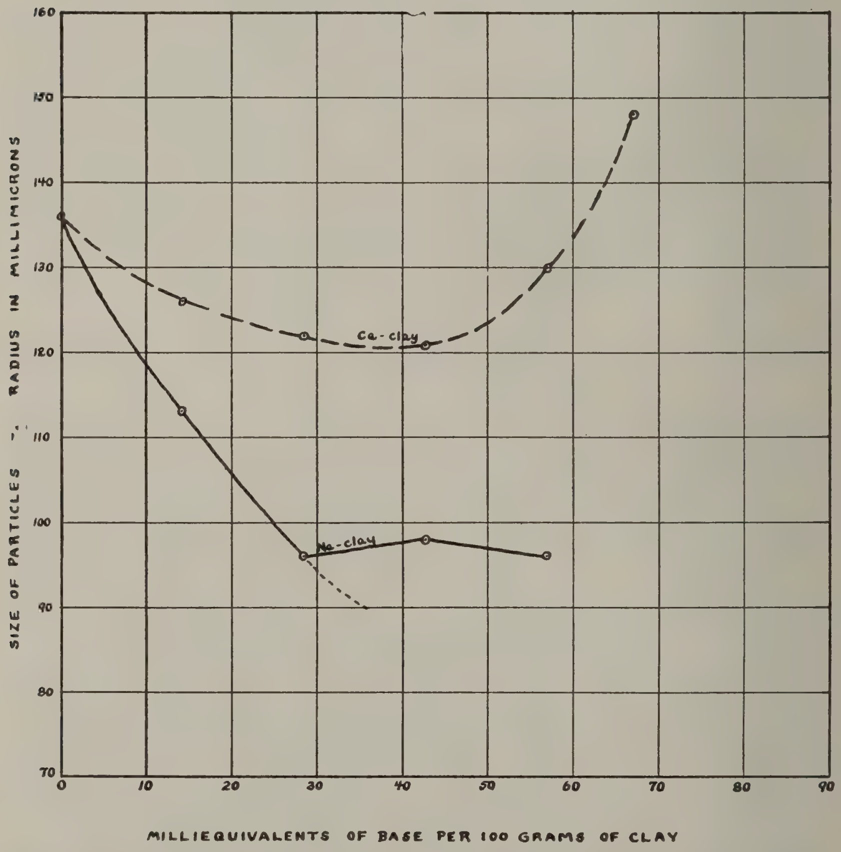

Fig. 6.—The effect of exchangeable Ca and Na upon the size of particles of colloidal clay

ultramicroscope that was employed in making the cataphoresis observations.

The results of these observations are given in Table 7 and Fig. 6. The average radius of the H-aggregate was found to be 136 millimicrons. The replacement of the H ions from the particles resulted in a dispersion of the aggregate since the average radius of the particles decreased. This decrease reached a minimum of 121 millimicrons with the Ca-clays when the particle was about 75 per cent saturated with this ion. Beyond this point the size of the particles increased, indicating a flocculating effect. The average radius of the Ca-aggregate was 148 millimicrons. The Na-ion caused a distinct change in the dispersion of the H-clay. The observed results seem to indicate that the maximum dispersion of this clay sol produces a particle having a radius of 96 millimicrons. However, the ultramicroscopic observations do not show the magnitude of this dispersion, probably due to the fact that many of the smaller particles resulting from this high degree of dispersion were not seen. It was very evident from the appearance and behavior of these suspensions that a much higher degree of dispersion was obtained. These counts show that the size of the extracted colloid is near the upper limit of the colloidal state.* Nevertheless, the results clearly show the differences in the effect of the monovalent and divalent cations on the size of the particles produced by the replacement of the H ions from the colloid.

Rate of Ultrafiltration

A large difference was observed in the rate of filtration of these various sols. The Ca-clays filtered much more rapidly than the Na. This different rate in the filtration velocity indicated a large difference in the size of the pores in the two clays. As filtration proceeds a layer of clay is deposited upon the collodion membrane which also serves as a membrane. The thickness of this clay membrane becomes greater as the volume of the ultrafiltrate increases. The rate of filtration of two clay sols, 50 per cent saturated with Ca and Na ions, was determined in order to ascertain the relative differences in the size of pores of the clay membranes.

50 cc of distilled water were passed through the membrane under a pressure of 100 pounds per square inch. The rate of filtration was observed to be constant, amounting to 0.0166 cc/sec. 100 cc of the Na-clay suspension were then filtered on the same membrane and the volume of the ultrafiltrate measured at 10 minute intervals. After all of the intermicellar liquid had been filtered from the Na-clay, the mem-

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*The suspensions contained some particles with a diameter of 600 millimicrons which were not removed during supercentrifuging because of the relatively high viscosity of the concentrated Na-saturated clay. For this reason the absolute values found by the ultramicroscopic method are larger than would be expected in a colloidal solution free from these larger particles but the changes produced by the different ions would not be appreciably altered by their presence.

TABLE 8.—A COMPARISON OF THE RATE OF ULTRAFILTRATION OF CA- AND NA-CLAYS UNDER A PRESSURE OF 100 POUNDS PER SQUARE INCH

Time in minutes	Volume of ultrafiltrate		
	Distilled water cc	Ca-clay cc	Na-clay cc
10	13.0	9.5	9.0
20	22.5	17.0	13.5
30	32.5	24.0	17.5
40	42.5	30.0	20.5
50	----	35.5	23.5
60	----	41.0	26.5
70	----	45.5	29.0
80	----	50.5	31.0
90	----	55.0	33.0
100	----	----	34.5
120	----	65.5	38.25
140	----	----	41.50
160	----	79.5	44.75
180	----	95.5	47.25
200	----	----	49.25
380	----	----	62.75
430	----	----	68.25
510	----	----	75.25

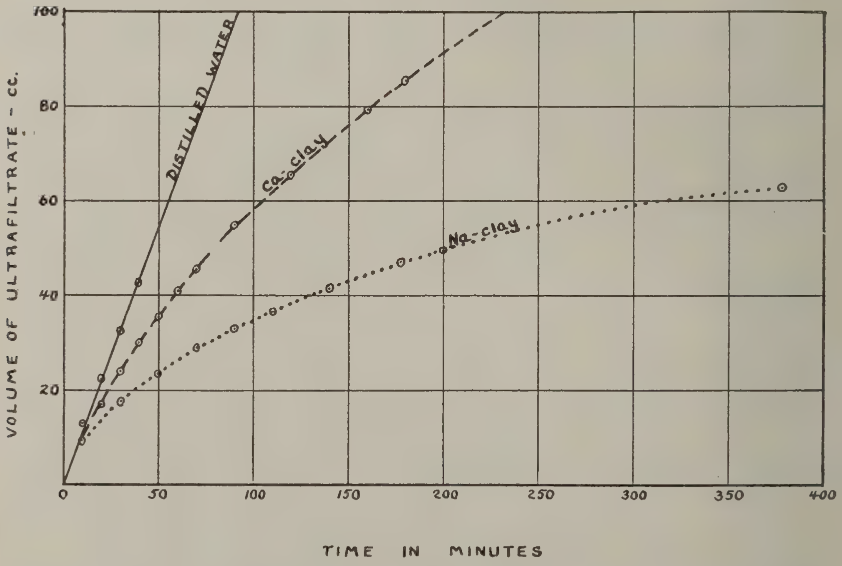

Fig. 7.—The effect of exchangeable Ca and Na upon the filtration velocity of clays.

brane was washed with distilled water and 100 cc of the Ca-clay filtered through it, making the observations at the same time intervals. Table 8 and Fig. 7 give the results of these observations.

It is quite evident from these data that the size of the pores in the Na-clay are much smaller than those in the Ca. The rate of filtration of the Na-sol decreases markedly as the colloid is deposited and the clay membrane is formed. This decrease in filtration velocity is not as pronounced with the Ca-sol. The size of the pores in these membranes were calculated according to the formula suggested by Bjerrum and Manegold[3] for determining the size of pores in collodion membranes. This formula is

$$r = \sqrt{\frac{8\eta dD}{w}} \qquad (8)$$

where

r = radius of the pore.
η = viscosity of the liquid.
d = thickness of the membrane.
D = permeability of the membrane for water per cm^2 in cm/sec., with a unit pressure of 1 cm of water.
w = per cent of water by volume in the membrane.

The per cent of water in the Na- and Ca-clay membranes after ultrafiltration was 96.4 and 95.85, respectively. The radii of the pores in the two membranes, calculated from this formula, were found to be 21.8 millimicrons for the Na-clay and 62.8 millimicrons for the Ca. The cross sections of the pores in the Na- and Ca-clay membranes were 1490 and 12400 square millimicrons, respectively. In other words, the relative size of the pores in the Ca-clay was 8.3 times greater than in the Na. The filtration velocity curves indicate that the Ca ion produces a porous structure, undoubtedly due to the nature and stability of the floccules formed.

VISCOSITY

Historical

Colloids are generally divided into two distinct groups, hydrophile and hydrophobe, with respect to their viscosity. Hydrophilic sols are characterized by a relatively high viscosity. The hydrophobic colloids do not possess a viscosity appreciably different from that of their dispersion medium. Clay sols can be considered as occupying an intermediary position, being neither truly lyophilic or lyophobic. Colloidal clay possesses the properties of hydrophilic colloids because of its hydration. Its sensitivity to electrolytes is a hydrophobic characteristic.

Viscosity measurements have been rather extensively used for the characterization of lyophilic colloids, even though most of the work has been more or less relative in nature. It has been fairly well established that the viscosity of colloids is a function of the volume occupied by the disperse phase. This volume should include that of the particle and any water of hydration that may be associated with it. Einstein[19] has proposed a formula showing the relation between viscosity and the volume of the dispersed phase. His equation indicates that any increase in viscosity in a colloidal system depends on the total volume of the particles and is independent of the degree of dispersion. This formula is

$$n_s = n_m \ (1 + 2.5 \ \Phi) \qquad (9)$$

where

n_s = viscosity of the colloidal system.
n_m = viscosity of the dispersion medium.
Φ = the volume of the dispersed phase per unit volume of sol.

This equation assumes that the particles are spherical and rigid. The value of Φ also includes any water of hydration associated with the particles. Modifications of this equation also include the relationship of viscosity to the volume of the dispersed phase. Emulsoid particles have a much larger "active volume" than that calculated from the size of the particle itself. This suggests that they are strongly hydrated. The nature of this hydration may be varied. Water may be held as a film around the particles by the forces of adsorption; it may be absorbed within the particle; or, it may be the result of hydration of the ions of an electrolyte that may be associated with the particle. Agar possesses a high degree of hydration and therefore a high viscosity. Oden[41] has shown that by increasing the degree of dispersion of his sulfur sol the viscosity increased. This was undoubtedly due to water adsorbed on the increased surface of the smaller sulfur particles.

Numerous investigators[12 20 28 36] have observed that the addition of small amounts of electrolytes to colloidal systems produces a sharp drop in their viscosity. Further additions either produce no change or cause an increase in viscosity, depending upon the nature of the colloid and the type of electrolyte. These viscosity changes appear to follow a course similar to that of the electrokinetic potential of colloidal systems.

There have been several theories proposed as an explanation of the nature of this decrease in the viscosity of colloids. The theories of Kruyt, Pauli and Wiegner will be considered here. Kruyt[31] bases his theory on Smoluchowski's modification of the Einstein equation. Smoluchowski[47], reasoning that the particles are electrically charged, thereby having a larger active volume, modified the Einstein formula as follows:

$$\frac{n_s - n_m}{n_m} = \frac{5}{2} \Phi \left[1 + \frac{1}{knr^2} \left(\frac{zD}{2\pi} \right)^2 \right] \qquad (10)$$

where

k = specific conductance.
r = radius of the particle.
D = dielectric constant of the medium.
z = electrokinetic potential of the double layer.

The original expression of Einstein is only valid for uncharged particles according to Smoluchowski's reasoning. He called this apparent increase in active volume of the particles the "quasi-voluminous effect". Kruyt, however, chooses to call it the "electro-viscous effect", by which is meant the increase in relative viscosity due to the electrical charge on the particles.

Kruyt and de Jong[32] showed that the viscosity of the agar sol decreased by removing its charge. This removal of charge depended entirely upon the valency of the added cation. The nature of the anion or cation played a minor part. De Jong[13] observed a decrease in viscosity with the starch sol to a minimum where further additions of electrolytes caused an increase in viscosity. He attributed the decrease to an electro-viscous effect and the increase to the lyotropic effect of the absorbed ions.

Eggink[17] studied the electro-viscous effect of rubber-benzene sols and found that the strength of the electrolyte, the degree of dissociation and therefore the actual concentration of cations played an important part in lowering the viscosity. Whitby and Jane[61] found that the effectiveness of acids in reducing the viscosity of rubber sols is in order of magnitude of their dissociation constants. They attribute this decrease to the electro-viscous effect arising from the neutralization of the charges on the dispersed phase by absorbed ions.

Pauli[43], on the other hand, in discussing the colloid chemistry of the proteins, attributes their physico-chemical properties to their degree of ionization. Likewise, their colloidal properties are dependent upon the same effect. Hydration of protein particles increases as ionization proceeds. This is concurrent with an increase in viscosity. Viscosity decreases as ionization is diminished. Since variations in viscosity are due to differences in hydration, he explains such differences by varied degrees of ionization of the protein salts. A similar hypothesis is advanced by Lewis and Daniel[35]. Thomas and Frieden,[52] explain the decrease in viscosity of the ferric oxide sol by the addition of $FeCl_3$ by analogous reasoning.

Viscosimetric determinations have been used by Wiegner[62], Gallay[22] and Demolon and Barbier[14] to study the changes taking place in the coagulation of colloidal clay. From a careful analysis of the data obtained, Wiegner[62] considers the hydration of ions as playing the important role in viscosity. Particles containing hydrated ions on their surfaces are voluminous and viscous in pure water. Those particles containing weakly hydrated ions around the primary particle have a lower viscosity.

The distribution of ions around the particle is considered as dependent upon the distribution of the different strongly hydrated ions such that those ions in the outside liquid draw water from the particle and the particle shrinks. Strongly hydrated ions within the particle draw water into the particle, producing swelling and therefore an increase in viscosity. The decrease and increase in the size of the particle is responsible for the viscosity changes. Wiegner's hypothesis is supported by the data of Gallay[22], stating that the hydration of particles is dependent on the nature of the ions in the exterior liquid and the nature of the adsorbed ions. In small colloidal particles combined water is considered not only a function of the capillaries but chiefly dependent on the chemistry of the clay surface and the hydration of electrolytes present[63].

Viscosity was found to increase during coagulation due to the hydration of the floccules. The viscosity of colloidal suspensions containing different ions adsorbed on the disperse phase decreases in order of the decrease in hydration of the respective ions. Viscosity is greater according to the progression: $Li > Na > NH_4$ and $K > Rb > Cs$ for the monovalent ions and $Mg > Ca > Ba$ for the divalent. Yoe and Freyer[63], in studying the effect of hydrogen-ion concentration on the viscosity of the hydrosols of aluminum, chromium and iron oxides, conclude that an increase in viscosity represents an increase in hydration. Demolon and Barbier[14] observed that the permeability of coagulated clay increased with the concentration of electrolytes. A distinct correlation was found between viscosity and permeability up to a certain maximum viscosity.

Measurements of viscosity of colloidal clay appear to give results that express fairly clearly changes in hydration and flocculation. These determinations may only produce relative data, nevertheless, with careful temperature control and a standardized technique, viscosity changes are indicative of certain hydration and structure changes in colloidal clay as produced by different adsorbed cations.

EXPERIMENTAL

A Washburn modification of the Ostwald type of viscosimeter was used in these determinations. The measurements were made in a thermostat regulated at 25° C. It required 46.2 seconds for water to flow through a fixed volume of the viscosimeter. 50 cc of each clay sol were placed in the viscosimeter and permitted to attain the temperature of the bath. The sol was thoroughly shaken in the viscosimeter before making each reading. A number of observations were made, agreeing within 0.2 of a second. Duplicate readings with the highly viscous, coagulated Li-, Na- and K sols did not check within about 5 seconds.

The efflux time for these clays was much greater than those that had not been flocculated.

DISCUSSION OF RESULTS

The results of these determinations are shown in Table 6 and Figs. 8 and 9. It is very evident that the monovalent and divalent cations exert entirely different effects on the viscosity of these clays. These effects may be explained as representing two types of hydration changes.

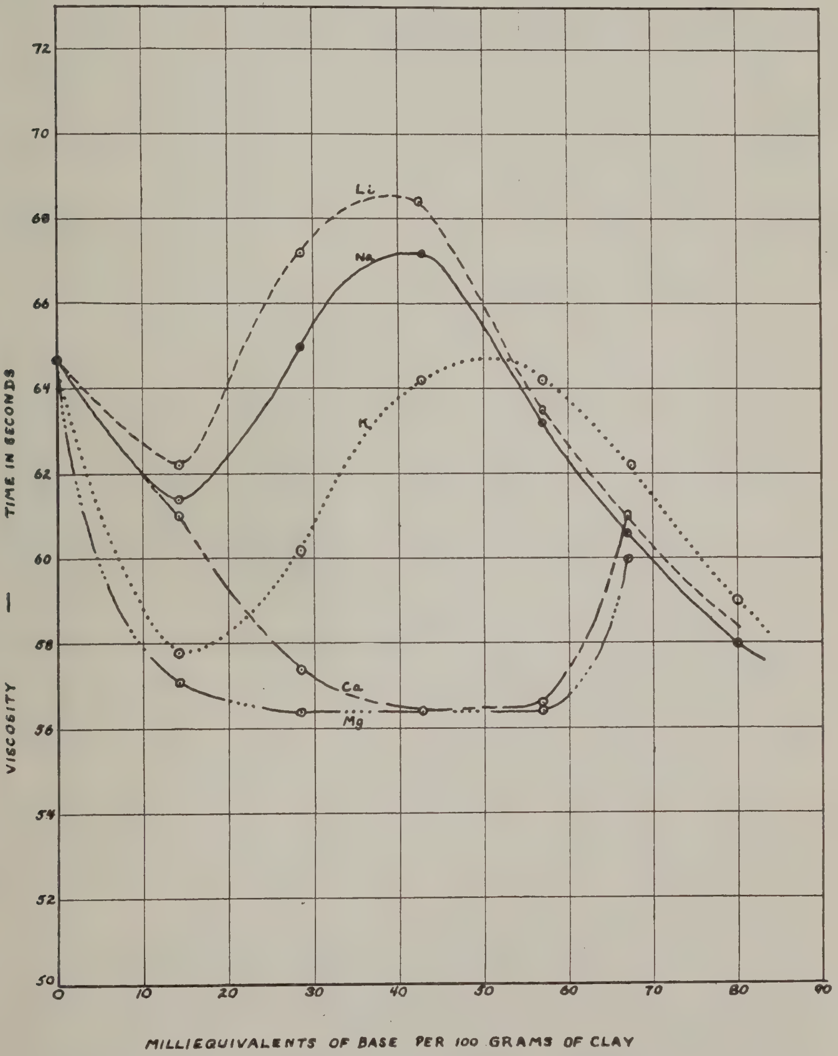

Fig. 8.—Viscosity of clay sols containing different amounts of bases.

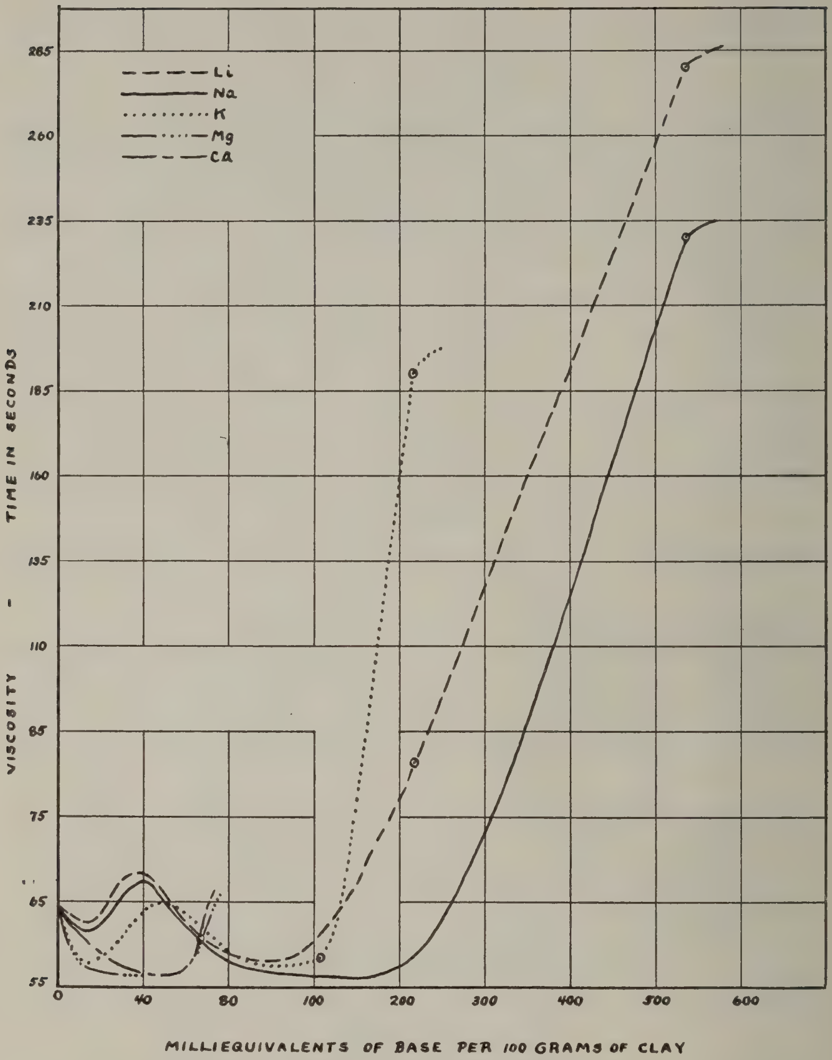

Fig. 9.—Viscosity of clay sols containing different amounts of bases.

Hydration of the system can be considered as being due either to a water film around the particle as produced by the absorption of highly hydrated ions, or, to water held between the particles in aggregate formation. Kuhn[34] classifies the latter type as occlusion water and the former as adsorption. Since the viscosity of a colloidal system is a function of the "active volume" of the dispersed phase, a colloidal aggregate, containing water enmeshed between the particles constituting the aggregate, will have a larger volume than the total volume of the individual particles. In other words, the volume of the aggregate will be the sum of the volume of the particles and the volume of the occluded water. Therefore, the aggregate will possess a higher viscosity than a suspension containing the same number of particles in a monodispersed state providing the dispersed particles contain no adsorbed water hull. On the other hand, if a highly hydrated ion is adsorbed by the particle,when the aggregate is dispersed, the volume of the particle will be larger, causing an increase in viscosity.

A careful study of the viscosity curves shows that both of these hydration effects occur with the monovalent ions. The H-saturated clay is not a monodisperse system. It is composed of loosely-bound, hydrated aggregates. The relative viscosity of this system is 1.4232. The addition of 14.25 milliequivalents of a monovalent base produces a marked decrease in viscosity. This decrease is the greatest with the K ion and least with the Li ion. The difference between the Li, Na and K ions is undoubtedly a lyotropic effect.

There are two opposing forces exerting their influence on the viscosity changes. Dispersion of the H-clay aggregate tends towards a decrease in the total volume of the dispersed phase and a decrease in viscosity. Hydration of the dispersed particles causes an increase in this volume and in viscosity. Therefore, the K ion, with the lowest hydration of the monovalent ions used, produces the least hydration of the particles, decreasing the viscosity the greatest. The high hydration of the Li ion, on the exchange complex, nearly counterbalances the effect of dispersion, inasmuch as the viscosity decreases only slightly. Thus, with only a slight addition of an exchangeable monovalent cation to this colloidal clay a distinct effect upon the viscosity and structure of the system is observed. The lyotropic effect of the cations is very obvious.

As the concentration of exchangeable monovalent cations becomes greater the viscosity increases to a maximum, then rapidly decreases to a minimum, increasing again as flocculation begins. This initial increase represents an augmentation in hydration as the concentration of the hydrated ions on the particle becomes greater. The charge on the particle and the dispersion of the system increases with the viscosity. The decrease in viscosity from the maximum point is accompanied by a sharp diminution of the migration velocity.

This maximum viscosity represents the point of largest hydration of the particle as produced by hydrated ions on the exchange complex. In other words, the exchange complex contains the largest number of cations functioning as active ions in the physico-chemical behavior of the colloid. That is, from the standpoint of hydration, viscosity, dispersion, migration velocity and other related phenomena dependent upon the activity of the ions on the surface of the particle, the maximum actvity should take place at this point. The colloid contains about 40 milliequivalents of exchangeable Li and Na and about 50 milliequivalents of K per 100 grams of clay at this point of maximum viscosity. The pH value of the suspensions containing these amounts of exchangeable monovalent cations is approximately 6.5 A distinct break occurs in the conductivity curves of these sols at the above values as shown in Fig. 2. The titration curves in Fig. 1. indicate an inflection point at the same place. However, the titration curves do not show the effect as markedly as the conductivity data.

The potentiometric and conductometric results show that the number of ions in solution, free from the surface of the colloid, increases rapidly above 50 milliequivalents of base per 100 grams of clay. This suggests that with a larger number of ions in solution, the concentration of ions on the particle exhibiting the property of hydration decreases. In other words, the Li-, Na- and K-clays begin to exhibit effects analogous to the hydrolysis of salts of weak acids. This effect has been reported by Bradfield[4] who attributes the acidity of soils to weak colloidal, aluminosilicic acids. Mattson considers a similar phenomenon occurring with Na-saturated clays inasmuch as the highly hydrated ions are least adsorbed and therefore more strongly dissociated.

These observations may be considered as analogous to a repression of ionization of the adsorbed ions at the same time repressing the hydration of the particle. Breazeale and McGeorge show that NaCl represses the ionization of a Na-zeolite back into an undissociated state. An alkaline soil that otherwise showed a large amount of OH ions in solution exhibited none whatever after the addition of NaCl. They observed the same effect with KCl. Wiegner[62] suggests that an increase in the concentration of electrolyte causes the outer layer of the colloidal particle, containing the exchangeable cations, to become tighter, decreasing the hydration of the particle. This repressing effect on the ions on the particle should be expected since conductivity measurements show an increase in the concentration of ions in solution.

The increase in concentration of ions in solution causes a corresponding decrease in hydration and viscosity to a minimum. Here an increase in viscosity occurs, although the experimental observations include only several points within this range. Nevertheless, as the concentration of cations increases, a point is reached where slow coagulation begins. As aggregation proceeds, water is enmeshed between the particles, and this hydration of the floccule causes an increase in viscosity. Table

6 and Fig. 9 show that the viscosity of Li-clay, containing 218 milliequivalents per 100 grams, is higher than the Na-clay containing the same amount of Na. The viscosity of the flocculated Li-clay is also higher than the Na, which in turn is greater than that of K. Thus, with the monovalent ions there are two types of viscosity corresponding to two types of hydration.

The divalent ions exhibit a different type of curve. There is a continuous decrease in viscosity until about 60 milliequivalents of Ca or Mg per 100 grams of clay have been added. At this point there is an increase in viscosity, undoubtedly due to the slow coagulation of the sol. The Ca- and Mg- sols flocculate with the addition of 67 milliequivalents, representing 117.5 per cent saturation of the colloid with these ions.

This continuous decrease in viscosity signifies a lowering of the hydration of the particles with respect to that of the original H-saturated aggregates. A diminution in the volume of the dispersed phase indicates that a replacement of the H-ions on the particle by Ca ions has caused at least a partial dispersion of the original aggregate. This is confirmed by ultramicroscopic counts as shown in Table 7 and Fig. 6. The radius of the H-aggregate was found to be 136 millimicrons. This size decreases with the concentration of Ca on the complex to a minimum of 121 millimicrons. These measurements undoubtedly include some aggregates. As flocculation proceeds the average size of the particles and aggregates increases. The electrokinetic potential of the system also decreases as shown in Table 6 and Fig. 5.

If the addition of small amounts of Ca ions to a H-clay maintained the original aggregate, viscosity would not be expected to diminish materially. Neither would there be a decrease in the size of the particles or aggregates. Therefore, the Ca ions must have partially dispersed the aggregate with the formation of particles occupying a smaller volume than those obtained in the dispersion of the aggregates by monovalent cations. The data appear to indicate that the replacement of H ions on the particle may proceed in two ways. One divalent cation either replaces two H ions from the same particle or one H ion from each of two adjacent particles. In the latter case, a doublet is formed. The divalent cation does not carry the water of hydration onto the particle and the total volume decreases, causing a diminution of viscosity. This connecting ion ceases to exert any influence on the system. Consequently, there is also a decrease in the electrokinetic potential of the particle, since a large particle is formed with a smaller number of ions exerting their influence on the charge on the particle.

Mattson[37] advances the idea that the particles absorb OH ions on the inner layer in the presence of hydroxides. The Ca ion joins the particles together by being attached to one hydroxyl ion from each of two particles. This process continues with the formation of a chain. When the aggregates become large enough the system flocculates. Similar views are held by Ehrenberg[18] and Hager[26]. Mattson claims that this effect takes place when the clay is treated with NaOH and a calcium salt, even though the potential of the system increases. These hypotheses, however, are more or less theoretical and lack sufficient experimental proof. Nevertheless, irrespective of the nature of this linkage, it appears logical to expect that a divalent ion can replace ions from two adjacent particles, especially when the particles are originally in contact in the form of loose aggregates. The effect of the Mg and Ca ions is practically the same. Hydration effects are not very evident.

It is interesting to note that the sols containing 67 milliequivalents of Ca and Li have the same viscosity. However, there is a distinct difference in the type of viscosity. The Li-saturated clay owes its viscosity to water of hydration produced by Li ions on the individual particles. The Ca-sol possesses a viscosity due to water enmeshed between particles during aggregation. In other words, the distinct effect of the highly dispersive monovalent cations as compared with the divalent ions is clearly shown at this one point.

The viscosity of the coagulated sols is greatest according to the ionic series: Li>Na>K>H>Ca and Mg. Jenny[29] studied the hydration of permutites saturated with different bases and found the series to be H>Li>Na>K. However, the SiO_2-sesquioxide ratio of his H-permutite was different from that of the other permutites. Gallay[22] observed that the Ca-soil possessed the lowest viscosity. Its floccules were dense and did not agglutinate because of their weak hygroscopicity. Ultramicroscopic observations show that the H-aggregate is smaller than that of Ca. From the standpoint of structure these two facts are of prime importance. The higher viscosity of the H-aggregate indicates a hydrated, loosely-bound system which is semi-reversible into the dispersed state. The Ca- and Mg-aggregates, however, are more stable, less hydrated and therefore less viscous. Demolon and Barbier[14] found that salts with a high flocculating power gave rise to large aggregates having a distinct rigidity and maximum permeability. Na-salts produced small, loose aggregates with a minimum permeability. Therefore, soils saturated with Ca and Mg would have a structure favorable for the movement of soil air and soil water. This structure would be fairly stable and not subject to fluctuations brought about by seasonal changes.

The size of the particles of the Na-clay sol was calculated from equation 10, involving Smoluchowski's conception of the electroviscous effect. Sols containing two different concentrations of cations are required in order to use this formula. The data for this calculation were taken from the Na-clay sols containing 57 and 67 milliequivalents of base per 100 grams of clay. Since the specific conductivity, viscosity and zeta-potential were determined experimentally, the radius of the particle was the only unknown. The average radius of the particle, including any water associated with it other than that produced by the charge on the particle, was calculated to be 249 millimicrons. The radius calculated from ultramicroscopic counts was approximately 96 millimicrons. The average radius of the pores in the Na-clay suspension containing 28.5 milliequivalents of base was calculated by equation 8 to be 21.8 millimicrons. The validity of Smoluchowski's equation involving the electroviscous effect has not been definitely confirmed experimentally. This value for the radius of the particles in this clay suspension is probably much higher than the true radius.

GENERAL CONCLUSIONS

These results as well as data taken from numerous investigators on the relation of electrolytes to the viscosity of colloids show without much question that viscosity changes are associated with changes in the degree of hydration of the particle. The nature of this hydration undoubtedly is a function of the ions adsorbed on the surface of the particle or of the water occluded between the particles in the case of aggregation. It appears logical to assume that changes in viscosity of colloidal systems is closely related to the physico-chemical properties of the substance stabilizing the system.

There appears to be an excellent correlation between the lyotropic series and viscosity changes in most colloidal systems. Wiegner's explanation of these changes is based entirely upon the hydration of the absorbed ions. Since differences in hydration are responsible for differences in viscosity, the hydration of the ions associated with the particle as well as those in the intermicellar liquid must play a significant part in the phenomena. If the hydration of ions is responsible for these effects, then the number of active ions in a system should be dependent upon the degree of ionization, or analogous phenomena, of the stabilizing ion. The ions in the non-ionized part of the system cannot be expected to exhibit hydration effects. Therefore, different colloids will show different viscosities due to variations in the ionization of some component of the system. Various degrees of ionization and unlike hydration of ions resulting from this dissociation will determine the viscosity of the system.

The results of this investigation upon the changes in the viscosity and the charge of colloidal clay as produced by increasing quantities of cations indicate that the theories of Kruyt, Pauli and Wiegner are not so widely different. The viscosity and migration velocity curves confirm the results of Kruyt. A definite electroviscous effect is exhibited as the concentration of cations increases above the saturation capacity of the colloid. From Pauli's point of view, this can be explained as being due to a decrease in ionization. Or, as suggested by Wiegner, there is a decrease in the hydration of the colloid. These data clearly point out the possibility of a more unified interpretation of the behavior of colloidal systems.

DISCUSSION

An analysis of the data obtained in this investigation indicates that the physico-chemical behavior of this colloidal clay is a function of the "active ions" on the surface of the colloid. The "active ions" are those ions which are dissociated from the particle. The non-ionized fraction of the total number of ions associated with the particle are considered as having no direct effect upon the properties of the system. Similar views are held by Pauli and his associates in their numerous investigations on the properties of various colloidal systems.

The monovalent cations exert varied effects on the properties of the system depending upon the amount and nature of the ion. The divalent ions always have a diminishing effect upon these properties. The maximum activity of the monovalent ions takes place at the point of saturation of the colloid with cations. This corresponds to 57 milliequivalents of base per 100 grams of colloid with this particular clay. Charge and viscosity of the clay increases with the monovalent ions to a maximum at this value, decreasing sharply as the concentration of cations increases beyond saturation. The maximum value obtained with any specific ion appears to be a function of the hydration of the ion. These changes may be explained on the basis of ionic equilibrium in the system. The substitution of monovalent ions for the H ions on colloid results in a dispersion of the loosely bound H-aggregates causing an increase in the charge and dispersion of the particles. Viscosity increases as a function of the hydration of ions on the particle. The breaks in the conductivity and titration curves of these suspensions coincide with the points of maximum charge and viscosity. The decrease in migration velocity and viscosity takes place as a result of an increasing concentration of cations in solution. These ions cause a repression of the ionization of the clay. This lower degree of ionization decreases the number of "active ions" in the complex and the physico-chemical activity of the system is diminished. The same effect is produced on the charge on the particles. This decrease in the viscosity curves may also be explained as an electro-viscous effect, as suggested by Kruyt, since there is a similar decrease in the charge on the particle.

The divalent cations have an entirely different effect upon the properties of the clay. A replacement of the H ion by Ca and Mg results in a continuous decrease in charge, hydration and viscosity. These relationships between divalent cations and the properties of colloids appear to be more or less universal. The hypothesis is made from an analysis of the viscosity curves and the values obtained for the size of the Ca-aggregates that a divalent ion probably not only exchanges two H ions from the same colloidal particle but also replaces one H ion from each of two adjacent particles. In the latter case a doublet is formed. The Ca ion disperses the H-aggregate as evidenced by ultramicroscopic counts. The viscosity decreases continuously up to about the saturation point as the concentration of the Ca ion increases. The charge on the particle also decreases. If the Ca ion produced aggregation viscosity should increase due to water enmeshed between the particles. The viscosity of the Ca-clay does not increase until flocculation begins which is slightly above its saturation capacity. The average size of the particles and aggregates becomes larger at the same point.

There appears to be no direct relation between the relative amounts of any particular cation on the colloid and the properties of the clay when compared with other ions. In other words, the properties of the system are not directly proportional to the degree of substitution of any one base for another. This is especially true in the comparison of the effects of the monovalent and divalent ions. The relations existing between the monovalent ions are somewhat similar. Mattson's results justify the same conclusion. Anderson, however, states that there tends to be a direct relation between the properties of colloidal clay and the degree of substitution of the various bases. However, as previously stated, the effect of the Cl ions in his clays may account for these differences.

The nature of the effects on the properties of this clay brought about by the Ca ion is of major importance in soil structure problems. It is fairly well conceded that granulation of a soil is concurrent with good structure. All attempts towards improving the physical condition of a heavy soil are based on the production of a granular structure. The Ca ion has always been used as the agent for producing this granulation. These results show that the Ca-aggregate is rather large, having a low viscosity. It is fairly well established that the Ca-aggregate is rather stable. This fact has been observed by the writer in a previous study as well as by other investigators. The H-aggregate is smaller and slightly more viscous indicating a higher degree of hydration and a lower stability. The aggregates produced by the monovalent ions are extremely viscous. The stability of the Ca-aggregate is of prime importance in the maintenance of any particular type of structure. Its stability is related to its low hydration, its low potential and probably to the union of particles as previously suggested.

Aggregation of colloidal clay takes place when the concentration of Ca is slightly above saturation. Conductivity data show an increase in the concentration of ions at this point, suggesting that the colloid must be saturated with Ca in order to maintain the maximum state of aggregation. As exchangeable Ca is replaced by the H ion, the complex breaks down into a higher degree of dispersion, producing a structure that is more or less reversible depending upon seasonal conditions. The fact that an excess of Ca ions above the saturation capacity of the colloid is required to produce flocculation is very important from the standpoint of an intelligent liming program on acid clay soils.

It was observed in a previous investigation on the relation of the different cations to the plasticity of soils, that the divalent ions increased the plasticity number by causing a distinct lowering of the lower plastic limit (that moisture content at which the soil can barely be rolled into a wire). The Na ion produced an increase in the plasticity number, both plastic limits being lowered. The K ion decreased the plasticity number, both limits being lowered. The large diminishing effect of the K ion was difficult to understand. However, the results of this investigation on the relation of the monovalent ions to the viscosity of this clay show that the difference in the effects of the Na and K ions is primarily a function of the hydration of the two ions. The K-clay has a lower viscosity than that of the Na. Likewise, it has a lower plasticity number. The Mg- and Ca-clays have lower viscosities than that produced by Na and K ions. However, their plasticity numbers are about the same as that of the Na-saturated soils but considerably higher than that of the K-soils.

These variations may be explained on the basis of the differences in the hydration of these clays. There are two types of hydration affecting the plasticity of these soils, just as there were two types of hydration affecting the viscosity of the colloidal clay, namely, water of hydration held between the particles in aggregate formation and the hydration hull around the particles. In order to produce plastic flow there should be an excess of water present above that required to satisfy the absorptive capacity of the particles or aggregates for water. The K-saturated soils will require less water to produce these plasticity effects than the Na-soils. This is merely a difference in the hydration of the particles as a function of the hydration of ions. The Ca- and Mg-sols require a certain amount of water to fill the pores in their aggregates. Therefore, a larger quantity of water is necessary to produce plastic flow than in the case of the K-saturated soils. The high hydration and dispersive action of the Na ion makes the plasticity of the Na-saturated soil greater than the soils saturated with the divalent ions.

The manifestation and stability of a given soil structure is probably a function of three variables. These variables are the clay content, the per cent of organic matter and the degree of saturation of the soil with calcium. The results with the heavy layer of the Putnam silt loam indicate that this colloidal clay must be about 117 per cent saturated with Ca in order to produce flocculation. This signifies that a favorable structure will be produced at this same value. The degree of saturation of a soil at which a good soil structure will be maintained will probably vary with the per cent of clay and organic matter.

Tiulin,[56],[57] considers the stability of soil structure to be directly dependent upon the degree of saturation of the soil with Ca. He uses a quantitative expression for the characterization of soil structure which he calls the "colloid-mechanical factor of stability of structure", This expression is

$$\frac{\text{Percent of silt in a soil}}{\text{adsorptive capacity in Ca}}$$

He found the aggregates formed by divalent ions to be stable, and nondiffusible in water. Aggregates held together by monovalent ions were instable, breaking up in an excess of water.

Undoubtedly, a good structure is associated with the ability of a soil to break up into aggregates and fragments that are stable under conditions of excess moisture. Ca-saturated soils have this property. Experimental investigations concerning the relations existing between the degree of saturation of the soil, its content of organic and inorganic colloids and certain well-defined types of soil structure will shed more light on the causes of these types of structure manifestation.

SUMMARY

1. Electrodialyzed Putnam clay was saturated to different degrees by titrating the H-clay with the hydroxides of Li, Na, K, Mg and Ca.
2. The saturation capacity of this clay was found to be 57 milliequivalents of base per 100 grams of clay.
3. The reaction of clay sols containing various amounts of the different cations was greatest according to the lyotropic series of cations: $Li > Na > K > Mg > Ca > H$.
4. The specific conductivity of this series of clay suspensions followed the order: $Na > Li > K > Mg > Ca$.
5. The flocculation values of the Li-, Na-, K-, Mg- and Ca-sols were 536, 536, 217, 67 and 67 milliequivalents of base per 100 grams of clay, respectively, using a 2.3534% by weight suspension.

6. The ultramicroscopic method of Tuorila was used for measuring the migration velocity of the colloidal particles. The velocity of the particles was found to be directly proportional to the fall in potential up to a potential gradient of 10 volts/cm. The velocity of the particles of H-clay increased with dilution. The monovalent cations increased the charge on the particles to a maximum at the saturation capacity of the colloid. The charge decreased as the concentration of ions increased beyond this point. Divalent cations decreased the charge. The critical potential for the Li-, Na-, K-, Mg- and Ca-clays was 38.2, 36.6, 34.0, 29.4 and 26.5 millivolts, respectively.
7. The average radius of the H-saturated particles and aggregates was 136 millimicrons, that of the Ca-aggregates being 148 millimicrons. The substitution of Ca and Na ions for H ions on the colloid resulted in a dispersion of the H-aggregate. The size of the pores in the Ca-clay were found to be much larger than those in the Na-clay.
8. Two types of viscosity and hydration changes were observed in these clay sols, (1) that due to water enmeshed between the particles in aggregate formation and (2) to water bound to the surface of the particle. In either case there is an increase in the total volume of the dispersed phase resulting in an increase in viscosity. The monovalent and divalent ions produced two different effects on the viscosity of the system. The former caused an initial decrease in viscosity, followed by an increase up to a maximum at the point of saturation of the colloid with cations. It decreased from this point to a minimum increasing again as flocculation took place. The divalent cations caused a decrease in viscosity to the point of flocculation where it increased sharply. The hydration and viscosity of the different clay aggregates were greatest according to the following order: Li>Na>K>H>Ca>Mg.
9. The changes in the physico-chemical properties of these clay sols are explained as being a function of the number of the "active ions" on the particle. Maximum activity occurs at the saturation capacity of the colloids for cations.
10. The size, stability and low hydration of the Ca- and Mg- aggregates are considered as important factors for producing and maintaining a good soil structure.

BIBLIOGRAPHY

1. Anderson, M. S., *The Influence of Substituted Cations on the Properties of Soil Colloids.*
   In Jour. Agr. Res., 38 (1929), pp. 565-584.
2. Baver, L. D., *The Relation of Exchangeable Cations to the Physical Properties of Soils.*
   In Jour. Amer. Soc. Agron., 20 (1928), pp. 921-941.
3. Bjerrum, N. and Manegold, E., *Über Kollodium-Membranen, II. Der Zusammenhang zwischen Membranstruktur und Wasserdurchlässigkeit.*
   In Koll. Zeit., 43 (1927), pp. 5-14.
4. Bradfield, Richard, *The Nature of the Chemical Reactions of Colloidal Clay.*
   In Colloid Symposium Monograph, 1 (1923), pp. 369-383.
5. Bradfield, Richard, *The Relation of Hydrogen-ion Concentration to the Flocculation of a Colloidal Clay.*
   In Jour. Amer. Chem. Soc., 45 (1923), pp. 1243-1250.
6. Bradfield, Richard, *Factors Affecting the Coagulation of Colloidal Clay.*
   In Jour. Phys. Chem., 32 (1928), pp. 202-208.
7. Bradfield, Richard, *The Saturation Capacity of Colloidal Clay Soils.*
   In Proc. First Int. Cong. Soil Sci., Washington, 4(1928), pp. 858-868.
8. Bradfield, Richard, *The Use of Electrodialysis in Physico-chemical Investigations of Soils.*
   In Proc. First Int. Cong. Soil Sci., Washington, 2 (1928), pp. 264-278.
9. Breazeale, J. F. and McGeorge, W. T., *Sodium Hydroxide rather than Sodium Carbonate in Black Alkali Soils.*
   In Ariz. Agr. Exp. Sta., Tech. Bul. No. 13, 1926.
10. Briggs, D. R., *The Zeta-potential and the Lyotropic Series.*
    In Jour. Phys. Chem., 32 (1928), pp. 1646-1662.
11. Buzagh, A. V., *Über Beziehungen zwischen elektrokinetischer Wanderungsgeschwindigkeit, Peptisation und Stabilität grobdisperser Systeme.*
    In Koll. Zeit., 48 (1929), pp. 33-43.
12. Chakravarti, D. N., and Dhar, N. R., *Viscosity Measurements of Certain Sols in the Presence of Electrolytes.*
    In Jour. Phys. Chem., 30 (1926), pp. 1646-1659.
13. De Jong, H. G., *The Electro-viscous Effect in Solutions of Soluble Starch.*
    In Rec. Trav. Chim. Pays-Bas, 43 (1924), pp. 189-202.
14. Demolon, A. and Barbier, G., *Contribution a l'etude de l'argile colloidäle.*
    In Ann. Sci. Agron., 44 (1927), pp. 341-373.
15. De Sigmond, A. A. J., *Beziehungen der sogennanten künstlichen Zeolithe mit den Basenaustausch und den physikalischen Eigenschaften der Alkaliboden.*
    In Proc. Fourth Int. Soc. Soil Sci., Rome, 2nd Com., (1924), pp. 434-444.
16. De Sigmond, A. A. J., *Hungarian Alkali Soils and Methods of Their Reclamation.*
    In Cal. Agr. Exp. Sta. Special Pub., 1927.
17. Eggink, A. N., *The Electro-viscous Effect in Rubber-benzene Sols.*
    In Rec. Trav. Chim. Pays-Bas, 42 (1923), pp. 317-331.
18. Ehrenberg, P., *Zur Bildung der Bodenkrumel und Ackergare.*
    In Landw. Ver. Stat., 99(1922), pp. 115-121.
19. Einstein, A., Cited by Kruyt (31), p. 167.
20. Farrow, F. D., *The Viscosity of Aqueous Solutions of Sodium Palmitate and the Influence of Electrolytes on the Same.*
    In Jour. Chem. Soc., 102 (1912), pp. 347-357.

21. Freundlich, H. and Abramson, H. A., *Über die kataphoretische Wanderungsgeschwindigkeit groberer Teilchen in Solen und Gelen.*
In Zeit. physik. Chem., 128 (1927), pp. 25-38.

22. Gallay, R., *Beitrag zur Kenntniss der Tonkoagulation.*
In Kolloidchem. Beih., 21 (1926), pp. 431-489.

23. Gedroiz, K. K., *Colloidal Substances in the Soil Solution. Formation of Sodium Carbonate in the Soil. Alkali Soils and Saline Soils.*
In Zhurnal Opitnoi Agronomii (Jour. Exp. Agron.) 13, (1912), pp. 363-412.

24. Gedroiz, K. K., *Rapidity of Reaction in the Soil. The Colloidal Condition of the Soil Saturated with Various Bases, and the Indicator Method of Determining the Colloidal Content of the Soil.*
In Zhur. Opit. Agron., 15 (1913), pp. 181-205.

25. Gedroiz, K. K. *Ultra-mechanical Composition of Soils and its Dependence on the Nature of the Cations present in an Absorbed Condition. Liming as a Measure of Improving the Ultra-mechanical Composition of the Soil.*
In Zhur. Opit. Agron., 22 (1924), p. 29.

26. Hager, G., *Bodenstruktur und Kolloidchemie.*
In Zeit. Pflanz. Dung. u. Boden., 2A (1923), pp. 292-311.

27. Hissink, D. J. *Base Exchange in Soils.*
In Trans. Faraday Soc., 20 (1925), pp. 551-566.

28. Hoffman, W. F. and Gortner, R. A., *Physico-chemical Studies on Proteins. I. The Prolamines—their Chemical Constitution in Relation to Acid and Alkali Binding.*
In Colloid Symposium Monograph, 2 (1924), 209-368.

29. Jenny, Hans, *Kationen- und Anionenaustausch an Permutitgrenzflächen.*
In Kolloidchem. Beih., 23 (1927), pp. 428-472.

30. Kelley, W. P. and Brown, S. M., *Base Exchange in Relation to Alkali Soils.*
In Soil Sci., 20 (1925), pp. 477-495.

31. Kruyt, H. R. (Translated by van Klooster, H. S.). *Colloids.* p. 83.
New York, John Wiley & Sons, 1927.

32. Kruyt, H. R. and de Jong, H. G., *Kapillarelektrische Erscheinungen an lyophilen Solen.*
In Zeit. physik. Chem., 100 (1922), 250-265.

33. Kruyt, H. R. and van der Willigen, P. C., *Über die Methodik der kataphoretischen Messungen bei Suspensoiden.*
In Koll. Zeit., 44 (1928), pp. 22-32.

34. Kuhn, A., *Überblick unserer jetzigen Kenntnisse uber Wasserbindung in Kolloiden.*
In Koll. Zeit., 35 (1924), pp. 275-294.

35. Lewis, W. K. and Daniel, C. F., *Mass Action Effects in the Interaction of Gelatine and Acids.*
In Colloid Symposium Monograph, 4 (1926), pp. 122-131.

36. Loeb, Jacques, *Proteins and the Theory of Colloidal Behavior.*
2nd Ed. New York, McGraw-Hill Book Co., 1924.

37. Mattson, S., *Die Beziehungen zwischen Ausflockung, Adsorption, und Teilchenlädung mit besonderer Berucksichtigung der Hydroxylionen.*
In Kolloidchem. Beih., 14 (1922), pp. 227-316.

38. Mattson, S., *The Relation Between the Electrokinetic Behavior and the Base Exchange Capacity of Soil Colloids.*
In Jour. Amer. Soc. Agron., 18 (1926), pp. 458-470.

39. Mattson, S., *Anionic and Cationic Adsorption by Soil Colloidal Materials of Varying* $SiO_2/Al_2O_3+Fe_2O_3$ *Ratio.*
In Proc. First Int. Cong. Soil Sci., Washington, 2 (1928), pp. 199-211.

40. Mattson, S., *The Influence of the Exchangeable Bases on the Colloidal Behavior of Soil Materials.*
In Proc. First Int. Cong. Soil Sci., Washington, 2 (1928), pp. 185-198.

41. Oden, Sven., *Physikalisch-chemische Eigenschaften der Schwefelhydrosols*
In Zeit. physik. Chem., 80 (1912), pp. 709-736.

42. Parker, F. W. and Pate, W. W., *Base Exchange in Soil Colloids and the Availability of Exchangeable Calcium in Different Soils.*
In Jour. Amer. Soc. Agron., 18 (1926), pp. 470-482.

43. Pauli, Wo., *Colloid Chemistry of the Proteins.*
London, J. & A. Churchill Co., 1922.

44. Pauli. W. and Schmidt, E., *Beiträge zur allgmeinen Kolloidchemie. XXII. Physikalisch-chemische Untersuchungen am Aluminumoxydsol.*
In Zeit. physik. Chem., 129 (1927), pp. 199-222.

45. Powis, F., *Die Beziehung zwischen der Bestandigkeit einer Ölemulsion und Potentialdifferenz an der Öl-Wassergrenzfläche und die Koagulation kolloider Suspensionen.* In Zeit. physik. Chem., 89 (1915), 186-212.

46. Rabinowitsch, A. J. and Dortmann, W. A., *Über die Elektrokoagulation der Kolloid.*II. *Konductometrische Verfolgung des Koagulationsprocesses von Arsentrisulfidsolen.*
In Zeit. physik. Chem., 131 (1927), pp. 313-337.

47. Smoluchowski, M. V., *Theoretische Bermerkungen über die Viskosität der Kolloid.*
In Koll. Zeit., 18 (1916), pp. 190-195.

48. Smoluchowski, M. V., Cited by Tuorila (59).

49. Sokolovski, A. N., *Beiträge zur Erkenntnis der Bodenkolloide und einige praktische Folgerungen davon.*
In Int. Mitt. für Boden., 13 (1923), pp. 81-98.

50. Sokolovski, A. N., and Lukaschewitsch, E. S., *Contribution to the Knowledge of the Physical Properties of Soils.*
Abst. in Int. Rev. Sci. and Prac. Agr., N. S. 4 (1926), pp. 338-341.

51. Svedberg, The., *Colloid Chemistry.*
New York, Chemical Catalog Co., 1924, p. 193.

52. Thomas, A. W. and Frieden, A., *Ferric Salt as the "Solution Link" in the Stability of the Ferric Oxide Hydrosol.*
In Jour. Amer. Chem. Soc., 45 (1923), pp. 2521-2532.

53. Thomas, M. D., *Aqueous Vapor Pressure of Soils. III. Soil Structure as Influenced by Mechanical Treatments and Soluble Salts.*
In Soil Sci., 25 (1928), pp. 409-418.

54. Thomas, M. D., *Replaceable Bases and the Dispersion of Soil in Mechanical Analysis.*
In Soil Sci., 25 (1928), pp. 419-427.

55. Thomas, M. D., *Aqueous Vapor Pressure of Soils. IV. Influence of Replaceable Bases.*
In Soil Sci., 25 (1928), 485-493.

56. Tiulin, A. Th., *Some Questions on Soil Structure. I. Dependence of the Stability of Soil Structure on Adsorptive Complex and Silt.*
Abst. in Proc. Int. Soc. Soil Sci., 4 (1929), pp. 49-51.

57. Tiulin, A. Th., *Some Questions on Soil Structure. II. Aggregate Analysis as a Method for the Determination of Real Soil Structure.*
Abst. in Proc. Int. Soc. Soil Sci. 4 (1929), pp. 51-54.

58. Tuorila, P. *Über Beziehungen zwischen Koagulation, elektrokinetischen Wanderungsgeschwindigkeiten, Ionenhydration and chemischer Beeinflussung.* In Kolloidchem. Beih., 27 (1928), pp. 44-181.
59. Tuorila, P., *Eine ultramikroskopische Methode zur Bestimmung der Lädungsgrosse kolloider Teilchen.* In Koll. Zeit., 44 (1928), pp. 11-22.
60. Valko, E. and Weingarten, N., *Beiträge zur allgemeinen Kolloidchemie. XXIV. Kolloidsalzleitfahigkeit und Kolloidionbeweglichkeit.* In Koll. Zeit., 48 (1929), pp. 1-10.
61. Whitby, C. S., and Jane, R. S., *The Electro-viscous Effect in Rubber Sols.* In Colloid Symposium Monograph, 2 (1924), pp. 16-28.
62. Wiegner, G., *Dispersität und Basenaustausch.* In Proc. Fourth Int. Soc. Soil Sci., Rome, 2nd Com., (1924), pp. 390-424.
63. Wiegner, G., Gallay, R., and Gessner, H., *Wasserbindung im Boden.* In Koll. Zeit. 35 (1924), pp. 313-322.
64. Wintgen, R. and Weisbecker, H., *Über das Säure- und Basenbindungsvermogen von Chromoxydsol.* In Zeit. physik. Chem., 135 (1928), pp. 182-198.
65. Yoe, J. H. and Freyer, E. B., *The Effect of Hydrogen-ion Concentration on the Viscosity of Hydrosols of Aluminum, Chromium and Iron Oxides.* In Jour. Phys. Chem., 30 (1926), pp. 1389-1400.
66. Zakharov, S. A. *Achievements of Russian Science in Morphology of Soils.* In Pub. No. 2, Russian Pedological Investigations, Pub. by Academy of Sciences, Leningrad, 1927.

BIOGRAPHY

Leonard David Baver was born at Miamisburg, Ohio, December 8, 1901. His parents, Mr. and Mrs. Amos Baver, lived on a farm where he received his early training. He was graduated from Miamisburg High School in June 1917. He entered Ohio State University in the fall of 1918, receiving his B. Sc. in 1923 and his M. Sc. in 1926 from this institution. He was married to Miss Mildred Gauger, New Philadelphia, Ohio in August 1928. He was employed as Assistant in Agronomy (Soil Physics) at the Ohio Agricultural Experiment Station, Wooster, Ohio, from July 1923 to September 1928, taking a leave of absence to accept a Research Fellowship in Soils at the University of Missouri. He resigned from his duties at Wooster to accept a position as Associate Soil Chemist at the Alabama Polytechnic Institute, Auburn, Alabama, beginning August 1, 1929.

He has been the author of five scientific articles during his five years of research work at the Ohio Station. These articles are:

1. The use of the quinhydrone electrode for measuring the hydrogen-ion concentration of soils. In Soil Sci., 21:167-179, 1926.
2. Factors affecting the hydrogen-ion concentration of soils. In Soil Sci., 23:399-414, 1927.
3. Mechanical dispersion as an aid in the chemical study of soils. In Jour. Amer. Soc. Agron., 20:403-410, 1928.
4. The relation of exchangeable cations to the physical properties of soils. In Jour. Amer. Soc. Agron., 20:921-941, 1928.
5. The drift in potential of the quinhydrone electrode. In Jour. Amer. Soc. Agron., 20:1125-1140, 1928.

He is a member of Sigma Xi, Gamma Sigma Delta, American Society of Agronomy, American Chemical Society, American Soil Survey Association and International Society of Soil Science.

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